

POLYMERIZATION OF C₆₀ WITH
METHYL METHACRYLATE
AND STYRENE

By

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PREFACE

The novel compound Buckminsterfullerene (C_{60}) consist of spherical molecules with atoms bonded together in 5- and 6-membered rings, as on a soccer ball. Since its discovery in 1985, research has shown some promising physical, electrical, and optical properties. Potential applications are still under investigation, but some possible uses might be found in superconducting devices, chemical sensors, and optical filters.

The long term goal of this research project is to incorporate C_{60} into thin films which will possess some of the same unique optical properties exhibited by C_{60} . Films can be made from polymer solutions or from polymer latexes. A latex is an aqueous dispersion of polymer particles produced by emulsion polymerization. An emulsion contains one phase dispersed into another, for example oil in water. However, C_{60} does not polymerize in an emulsion due to its poor solubility in monomer. Therefore, C_{60} was first derivatized with a monomer in a solution polymerization in order to improve its solubility. A solution polymerization uses a solvent that will dissolve both C_{60} and the monomer. Polymerization gives a copolymer containing C_{60} and monomer that has much better solubility properties than C_{60} itself and can be used in emulsion polymerization to obtain a latex with C_{60} copolymer dispersed in the aqueous phase.

This thesis discusses the syntheses of C_{60} copolymers by solution polymerization. The products were analyzed to determine if polymerization occurred and how incorporation of C_{60} affected the molecular weights. C_{60} and methyl methacrylate or styrene were copolymerized using a free radical initiator. Control reactions were done in absence of C_{60} . Results indicate that C_{60} was copolymerized to form soluble products, and molecular weights of the C_{60} containing products were lower than corresponding products synthesized without C_{60} .

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CHAPTER I

INTRODUCTION

Background. A new era in carbon chemistry began in 1985 when Kroto and Smalley detected the caged-shaped sixty carbon compound called buckminsterfullerene.¹ The compound has also been called buckyball, C₆₀, or simply referred to as fullerene. The fullerenes are actually a family of caged-shaped all carbon homologues. However, in this manuscript, the term will refer only to buckminsterfullerene.

When Kratschmer and Huffman published a procedure in 1990 for the isolation of gram quantities of C₆₀, research into the unique properties of this fascinating compound began to explode.² Since their original publication, other similar methods have been used to produce C₆₀, but none have been as widely used as the Kratschmer-Huffman method.³

The number of C₆₀ publications has exceeded 2,500, but an uncertainty of its practical importance still lingers.⁴ From the intense research efforts put forth early on, it was discovered that C₆₀ possessed many intriguing properties such as superconductivity⁵, when in the form of its alkali metal salt M₃C₆₀, and promising nonlinear optical properties.⁶

The C₆₀ structure contains both five- and six-membered rings which creates two different types of bonds as shown in Figure 1.⁷ The first bond is located between two six-membered rings ([6,6]-bond) and the other between a five- and six-membered ring ([5,6]-bond). An x-ray crystal study of an osmate derivative proved the [6,6]-bond has more double bond character (*ca.* 1.39 Å) and the [5,6]-bond has more single bond

character (*ca.* 1.44 Å).⁸ The strongly bond-alternating structure dictates the reactivity of C₆₀.⁷

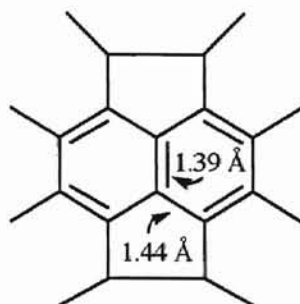


Figure 1. Five- and six-membered rings in C₆₀.⁸

Reactions of C₆₀. Initially, it was thought that C₆₀ was relatively unreactive. Now, it is known that C₆₀ is multifunctional and reacts with elements across the periodic table, which makes for a versatile repertoire of chemical reactions.^{9,10} C₆₀ is distinctly electrophilic so it undergoes nucleophilic additions with neutral and charged species such as organolithium and Grignard reagents, and primary and secondary amines.^{9,10} However, electrophilic additions involving halogens, carbenes, and free radicals have also been reported.^{9,10}

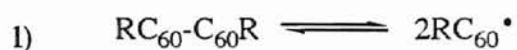
C₆₀ also has the capability of participating in cyclization reactions--one of the better methods for derivatizing C₆₀. It reacts with a variety of dienes such as anthracene, furan, isobenzofuran, p-nitrophenyl azide, and cyclopentadiene.^{9,10} A few dipolar compounds, such as ethyl diazoacetate, diphenyl diazomethane, and benzyne form cycloadducts with C₆₀.^{9,10}

Reactions with transition metal compounds such as osmium tetroxide and platinum complexes are known to occur.¹⁰ Incidentally, it was the reaction of C₆₀ with OsO₄ that produced the first characterizable derivative. The x-ray study of this osmyl ester provided the first conclusive proof of the C₆₀ framework.^{8,10} The platinum complex, [(L)₂Pt]₆C₆₀, has six metals positioned octahedrally around the C₆₀ core.^{10,11}

The sensitivity of C₆₀ to oxygen has been well documented in the literature.¹²⁻¹⁵ Cox and Smith were able to isolate an epoxide C₆₀O by UV irradiation of C₆₀ in benzene. Apparently, the spherical cage is not destroyed because the fullerene epoxide can be converted back to C₆₀ using alumina chromatography.¹² Conversion products such as C₆₀O₂ and C₆₀O₄ have been detected from the photodegradation of solid C₆₀¹³, and oxidation to CO and CO₂ occurs by high energy photoexcitation of C₆₀ in the presence of oxygen.¹⁴

Another interesting interaction between C₆₀ and oxygen was revealed by Colligiani and Taliani.¹⁵ Their research suggested that free radicals originate from the reaction of C₆₀ with molecular oxygen in the air based on electron spin resonance (ESR) analysis of toluene-C₆₀ solutions. However, the species generating the ESR signal could be removed upon filtration; therefore, the radicals were not truly in solution but existed as suspended microclusters.¹⁵

Free radical reactions of C₆₀. ESR has been used extensively to investigate the reactions of free radicals with C₆₀.¹⁶⁻²¹ The reactions occur rapidly, and multiple additions are common since the thirty carbon-carbon double bonds enable C₆₀ to act as a "radical sponge".¹⁶ From these reports, three things are now evident: the unpaired electron is restricted to the two fused six-membered rings with the substituent group on the other side of the [6,6]-bond¹⁷ (Figure 2); dimerization readily occurs with



monoadducts (equation 1)¹⁸; and the bond connecting the substituent group to C₆₀ is restricted, thereby, hindering rotation.¹⁹

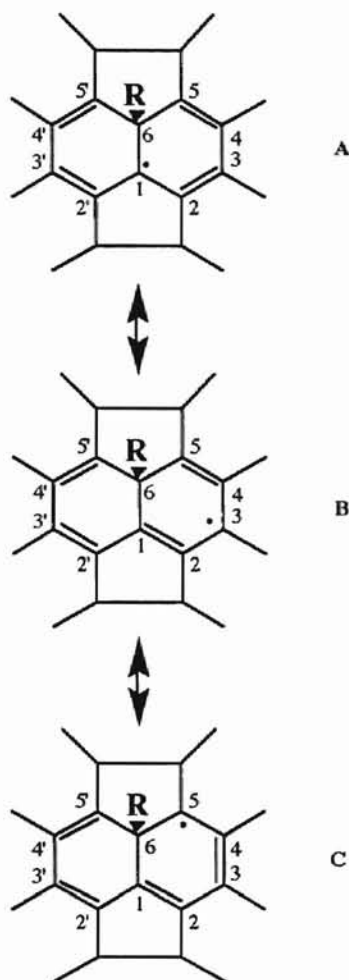
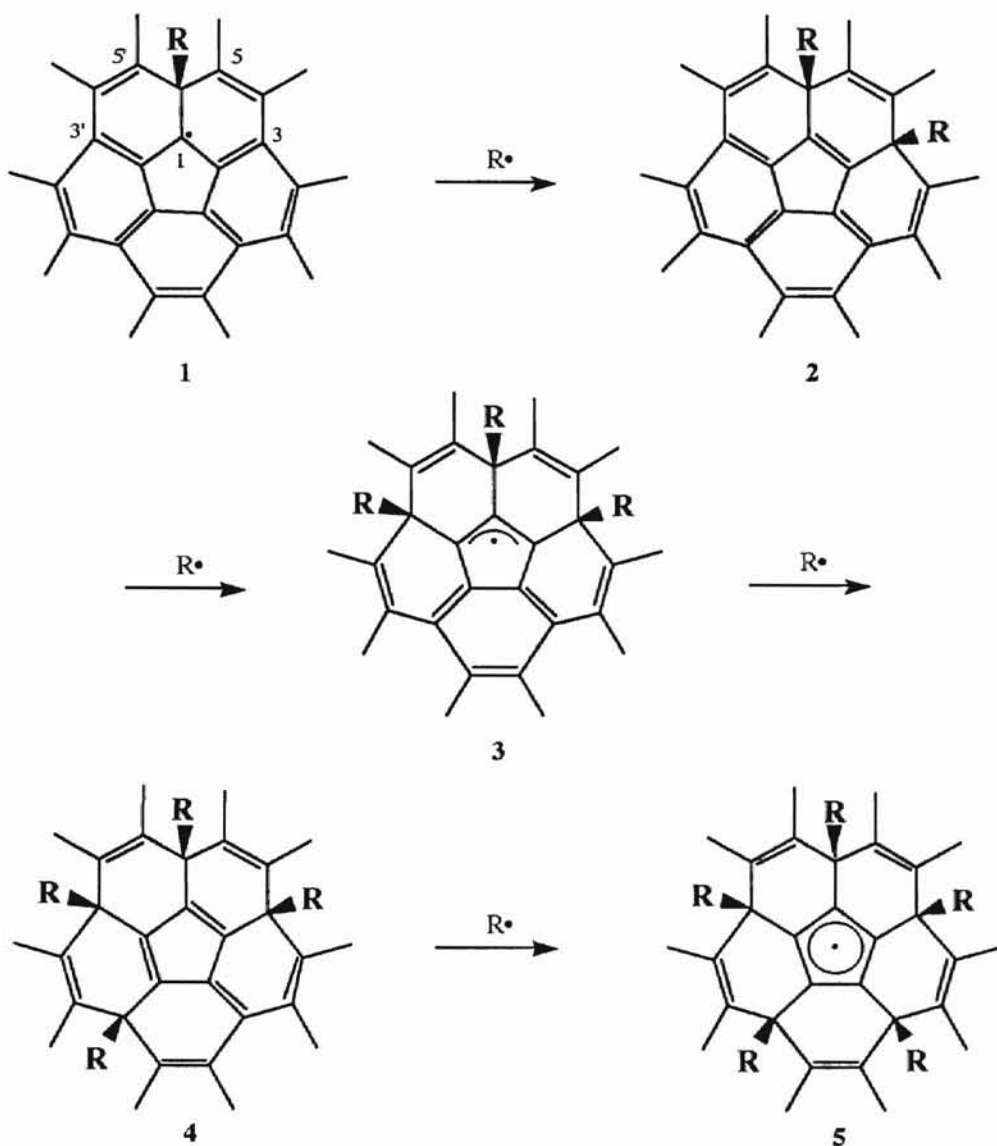


Figure 2. The five major canonical forms of R-C₆₀• radicals (**B** and **C** are doubly degenerate).²¹

In 1991, Krusic and co-workers¹⁷ reported that photochemically generated benzyl radicals add to C₆₀, producing radical and nonradical adducts C₆₀(CH₂C₆H₅)_n with n = 1 to 15. The benzyl radicals were formed by reaction of t-butoxy radicals with toluene. The first radical adds to C₆₀ to form the radical adduct **1** in Scheme I. The second radical adds to C3 in order to avoid unfavorable 1, 2-interactions. The newly formed double bond of nonradical **2** is partially conjugated with two other olefinic bonds; therefore, it becomes the preferred site of attack by the third radical to give an allylic radical (**3**) that is resonance and sterically stabilized. Further radical addition gives compound **4**, which forms the resonance stabilized cyclopentadienyl radical **5** upon addition of another

Scheme I. Radical formation.¹⁷

radical. Krusic was not able to rule out the possibility of similar structures elsewhere on the C₆₀ surface. The five carbons surrounding radical **5** equally share the unpaired electron. For radicals **3** and **5**, the steric hindrance of the benzyl group shelters the radical, thus, providing the stabilization of the unpaired electron. This same study also showed methyl radical addition to form C₆₀(CH₃)_n adducts with n = 1 to 34. The higher

reactivity of the methyl derivatives is due to the lack of steric hindrance providing accessibility to the radical site.¹⁷ Other reports have shown that fluoroalkyl, alkylthio, and alkoxy radicals also add to C₆₀.²⁰

Using one equivalent of radical precursor and at a stage early in photolysis, primary radical adducts, RC₆₀•, have been observed for several alkyl radicals.²¹ ESR was used to detect the mono radical adducts formed from reaction of *tert*-butyl, 1-adamantyl, isopropyl, ethyl, and benzyl radicals with C₆₀. The ¹³C hyperfine interactions of the ESR spectrum imply that the unpaired electron is confined on two fused, six-membered rings of the C₆₀• sphere as seen in Figure 2. This illustration represents the five major canonical forms of RC₆₀ radical which is analogous to a cyclohexadienyl radical. Delocalization of the radical over the C₆₀ sphere was ruled out based on weak intensities of ¹³C splittings.²¹

ESR also provided evidence for dimerization of mono radical adducts with bulky substituents such as CCl₃, (CH₃)₃C, or (CH₃)₂CH.¹⁸ The intensity of the ESR signals shows an unexpected increase with increasing temperature. The temperature dependence suggest that the radical is in equilibrium with its dimer. A correlation of the size of R and the change in enthalpy values was also discovered. As the substituent group becomes larger the ΔH decreases in equation 1. Therefore, the strength of the dimer bond depends on the degree of steric hindrance between the two substituent groups. As a result of steric hindrance, the dimer bond is believed to occur at C3-C3 since C1 and C5 are probably too close.¹⁸ Figure 3 provides a illustration for the *tert*-butyl-C₆₀ dimer.

Furthermore, ESR spectra revealed substantial barriers to rotation about the bond connecting the alkyl group to the C₆₀ core.¹⁹ By analyzing the temperature dependent shape of the lines and the hyperfine interaction of the ¹H and ¹³C spectra, an activation energy of 8.2 kcal/mol was obtained for bond rotation in the *tert*-butyl-C₆₀ adduct.^{19a}

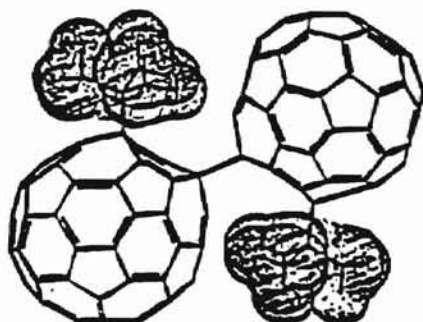


Figure 3. Molecular model of the dimer $[t\text{-butyl-C}_{60}]_2$.¹⁷

Polymers of C₆₀. A large number of fullerene derivatives have been reported at present. However, it wasn't until 1992 that publications of polymeric C₆₀ derivatives first appeared, and since then there have been several other articles addressing macromolecular modification of C₆₀.^{22,23} Polymeric derivatives are of great interest because the properties of specific polymers can be combined with those of C₆₀.

Basically, there have been two principal approaches to preparing fullerene containing polymers.²² One way is to start with C₆₀ or some monomeric derivative of C₆₀. The other method involves the reaction of preformed precursor polymers with C₆₀ or a derivative. The result of the latter procedure is a fullerene polymer derivative with an unchanged degree of polymerization.

As with many other types of reactions involving C₆₀, multiple products may be formed. However, the reactions usually produce three major types of polymer products:^{22,23} C₆₀ connected as a pendant group onto the polymer backbone or incorporated into the side-chains (on-chain); C₆₀ functionality incorporated into the polymer backbone (in-chain); and matrix modification. Matrix bound polymers include the covalent attachment of C₆₀ to surfaces of crosslinked resins, gels, and inorganic substrates. Graft copolymers, dendritic, and star-shaped derivatives are considered

important intermediates. Additionally, combinations of these types are possible. Figure 4 provides a classification of macromolecular derivatives of C_{60} .²²

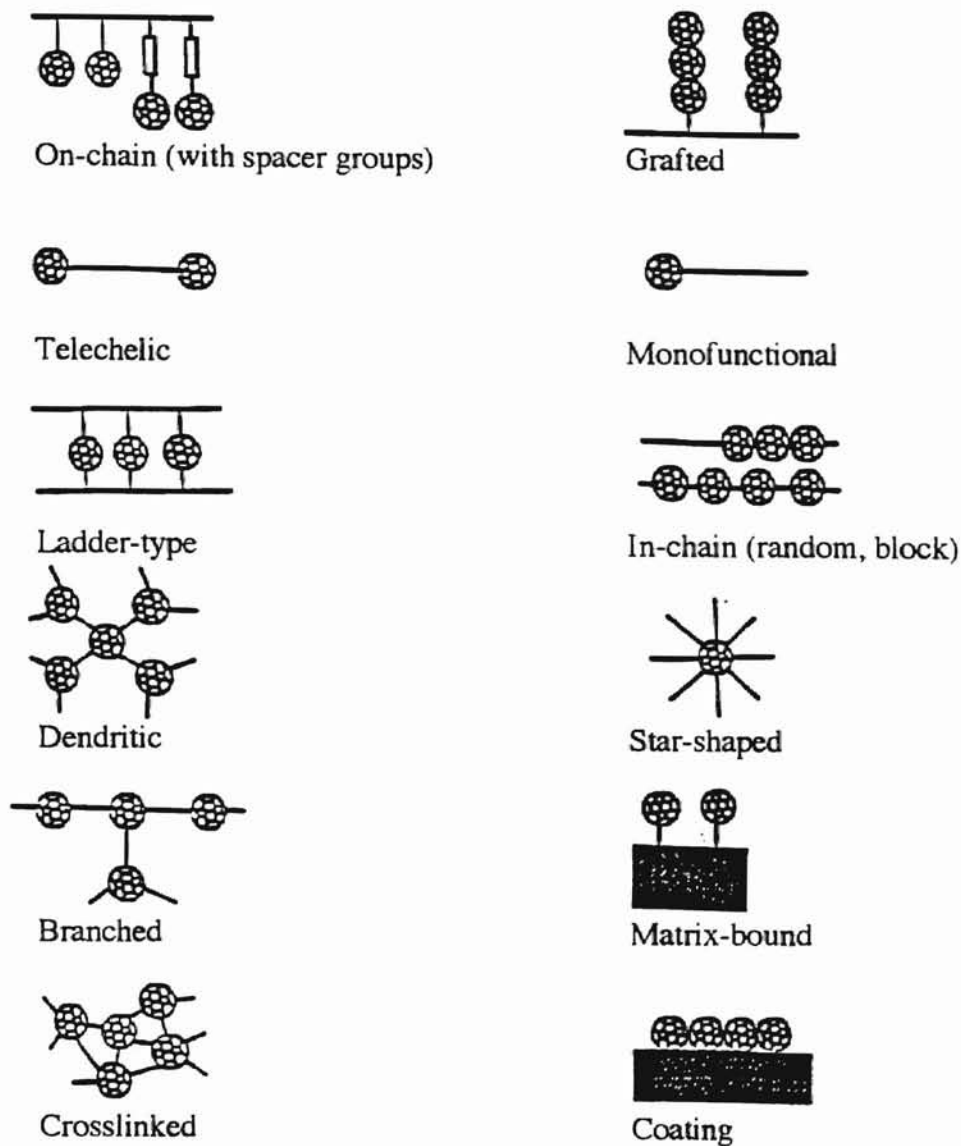


Figure 4. Classification of macromolecular derivatives of C_{60} .²²

Two problems associated with C_{60} polymerization reactions have been low molecular weight products and insolubility due to crosslinking. Suitable products should be processable either by spin-coating, solvent-casting, or melt extrusion.²² A summary of molecular weights and solubility of polymers that have been reported in the literature is provided in Table I.

Table I. Polymer derivatives of C₆₀.

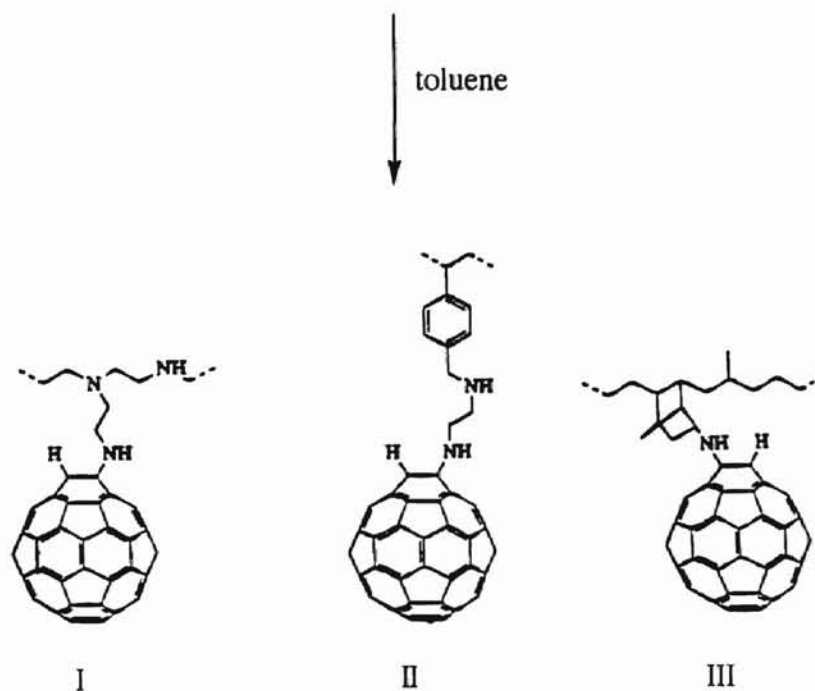
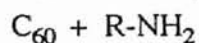
Structure	C ₆₀ Content	Molecular Weight	Comments	Solubility
Sch. II (I)	18:1 ^a	3.5 x 10 ³	Molar mass of preformed polymer.	No
Sch. II (II)	19:1 ^a	2.0 x 10 ⁴	Molar mass of preformed polymer.	Toluene, Carbon Disulfide
Sch. II (III)	NR ^b	2.0 x 10 ⁴	Mw of preformed polymer.	Tetrahydrofuran, Heptane
Sch. III	Up to 27%	1.5 - 4.3 x 10 ⁴	Determined by SEC.	Tetrahydrofuran
Sch. IV	5.5 - 29%	2.7 - 3.85 x 10 ³	Determined by SEC.	Chloroform, Tetrahydrofuran
Sch. V (I)	NR	4.0 x 10 ³	Determined by SEC.	Nitrobenzene, Benzonitrile
Sch. V (II)	NR	4.0 x 10 ³	Determined by SEC.	No
Sch. VI	NR	< 2.0 x 10 ³	Determined by FAB mass spectroscopy.	Chloroform
Sch. VII	3.4:1 ^c	NR		No
Sch. VIII	0.8:1 - 30:1 ^a	< 2.0 x 10 ³	Determined by SEC.	Chloroform
Sch. IX	100:1 ^a	1.5 - 3.4 x 10 ³	Determined by SEC.	Toluene, Water ^d
Sch. X	2:1 ^e	NR		Tetrahydrofuran
Fig. 5 a	NR	2.0 x 10 ⁴	Reported as Mw.	Dimethyl Sulfoxide, 1-Methyl -2-pyrrolidinone
Fig. 5 b	NR	5.0 x 10 ³	Reported as Mw.	Tetrahydrofuran, Dimethyl Sulfoxide
Fig. 5 c	NR	NR		No
Fig. 7	100%	1.4 x 10 ⁴	Laser desorption mass spectroscopy.	Isodurene (boiling) ^f

^a Molar ratio of polymer:C₆₀. ^b Not reported (NR). ^c Ratio of xylylene:C₆₀. ^d Some insoluble materials were formed under certain conditions. ^e Ratio of dendrimer:C₆₀. ^f Polymer is toluene insoluble.

On-chain polymers have been the best way of obtaining high molecular weight products, because it is fairly easy to start with preformed polymers that have a sufficient chain length.²² For example, soluble, low molecular weight amines are capable of reacting with C_{60} to form polymeric fullerene compounds. These reactions require mild conditions and are conducted at room temperature. An advantage of using this approach is the aminopolymers can be tailored. The solubility and functionality are systematically controlled by various constructions of the polymer backbone.²²

Scheme II shows the covalent attachment of some amine containing flexible hydrocarbon polymers with C_{60} to obtain solvent processable products.^{24,25}

Scheme II. Covalent attachment of C_{60} to amino polymers.^{23,24,25}

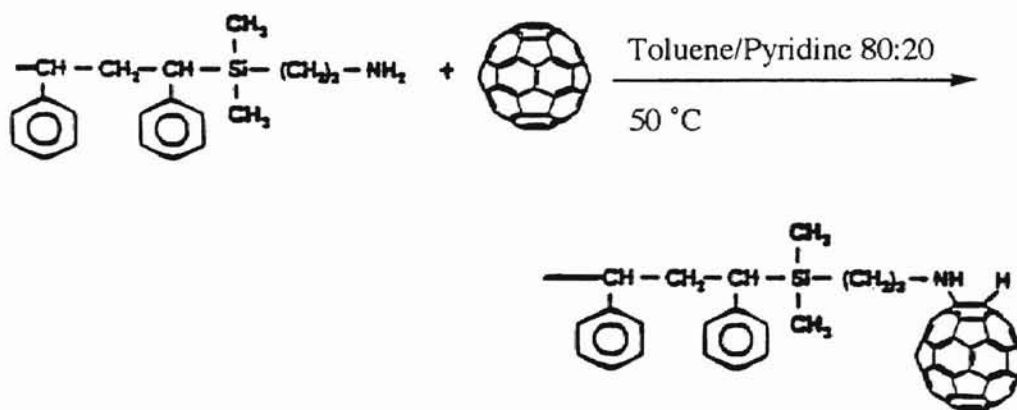


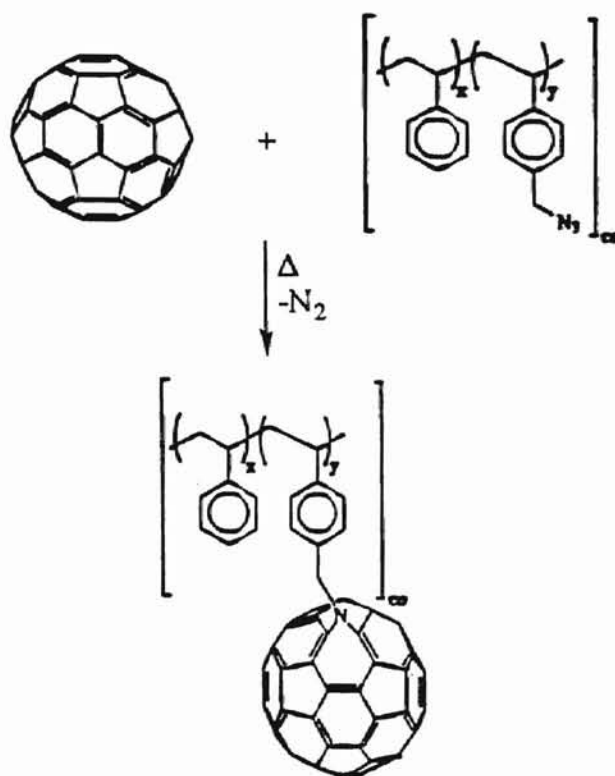
The polymeric derivatives **I** and **II** were determined to be monofunctionalized so they have electronic properties very similar to C_{60} .²⁵ These monofunctionalized

organofullerenes show peaks at 308, 326, 435 nm in the UV/Vis spectrum and splitting in the 580 to 514 cm^{-1} region of the IR. The incorporation of C_{60} into compound **III** was determined by infra-red spectroscopy. C_{60} peaks at 527 and 578 cm^{-1} along with an unfunctionalized polymer peak at 615 cm^{-1} disappeared upon reaction. However, these peaks were present in a mixture of C_{60} and amine polymer.²⁴

Another example in Scheme III involves an amino-terminated polystyrene which reacts with C_{60} to produce the homogenous and easily processable C_{60} end-capped polystyrene.²⁶ A simple and versatile method for creating C_{60} polymers can be accomplished via cycloaddition reaction of azido substituted polystyrene with C_{60} ²⁷ (Scheme IV). This route gives a processable polymer that retains the electronic properties of the C_{60} moiety. Size-exclusion chromatography and ^{13}C NMR were used to determine the covalent attachment of C_{60} for both methods presented in Scheme III and IV. The ^{13}C spectra show a broad set of resonance between 133 and 148 ppm, and the C_{60} peak (143 ppm) is absent.

Scheme III. Formation of C_{60} end-capped polystyrene.²⁶

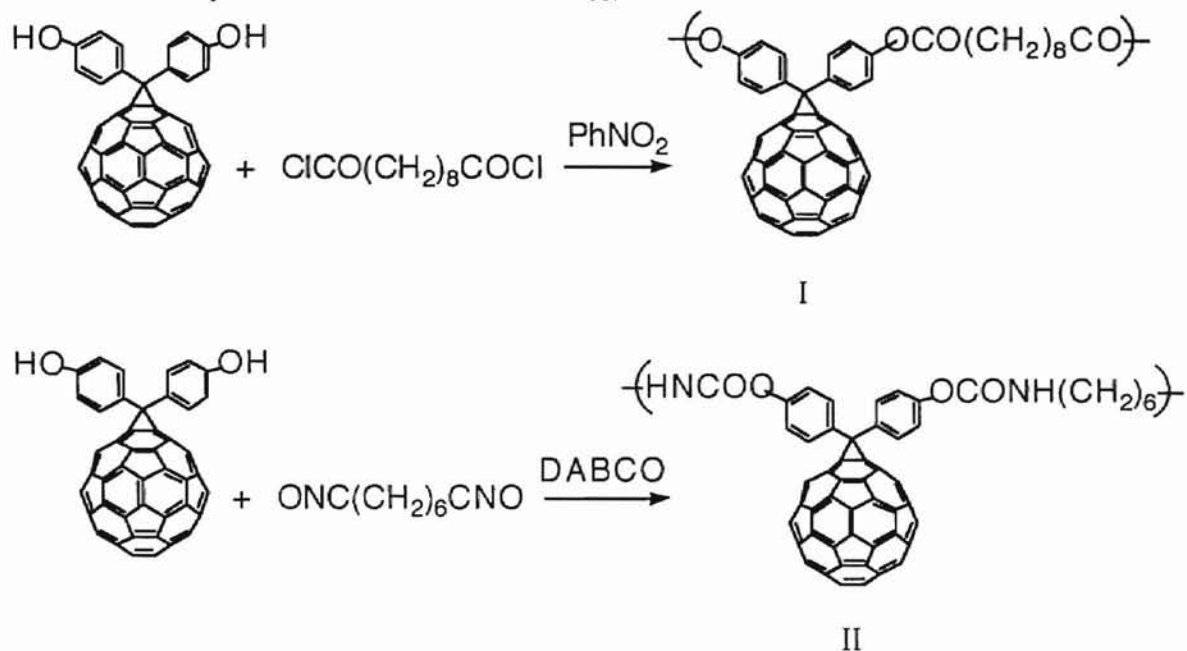


Scheme IV. Cycloaddition reaction of azido polystyrene with C₆₀.²⁷

On-chain polymers can also be produced by starting with derivatized C₆₀ as the monomer. Polycondensation reactions of a fulleroid (HOC₆H₄)₂C₆₁ with sebacoyl chloride or hexamethylene isocyanate were conducted to prepare charm-bracelet-type polymers.^{22,23,28} The products obtained from this reaction were an insoluble urethane (**II**) and a soluble ester derivative (**I**) as shown in Scheme V. The insolubility of the urethane is due to crosslinking. Interestingly, the UV-vis spectroscopic data and cyclic voltammetry results revealed that the electronic properties of C₆₀ were retained for both products. The FTIR spectrum of the product was essentially the same as the starting C₆₀

derivative. The polymers were reported to have a low molecular mass of 4000 g/mol. This leads to the conclusion that the polymer must consist mainly of short oligomers, because the fulleroid monomer itself contributes 720 amu.²⁸

Scheme V. Polycondensation reactions of C₆₀.²⁸



Fulleroids have also been used to synthesize soluble polysulfones²⁹ and the polymeric carbon allotrope in Figure 5.³⁰ However, the covalent incorporation of C₆₀ has not been proven.

In-chain polymeric fullerene derivatives are obtained by using unfunctionalized C₆₀ as a monomer in the polymerization reactions. One disadvantage to this approach is the difficulty in controlling the reaction and products.²² Some selected examples of in-chain polymers are given in the following paragraphs.

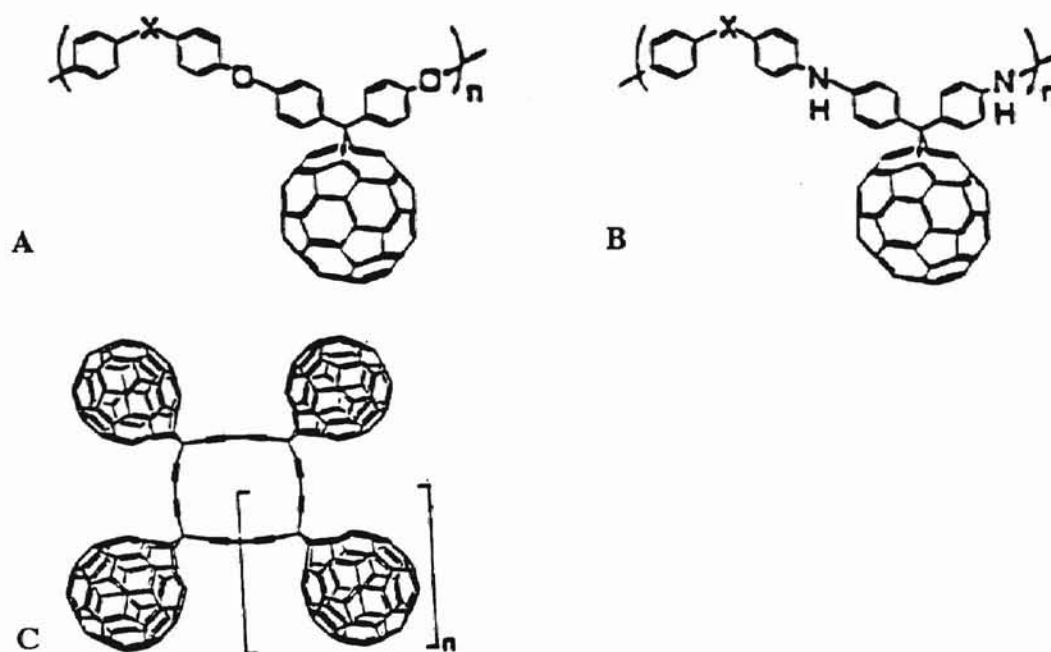
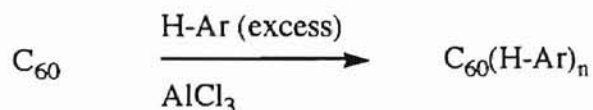


Figure 5. Polysulfones (A and B, $x = \text{SO}_2$)²⁸ and polymeric carbon allotrope (C).³⁰

C_{60} undergoes Friedel-Crafts acid catalyzed addition with benzene or toluene to produce polyarenefullerenes $\text{C}_{60}(\text{H-Ar})$ (Scheme VI). On average, there are twelve H-Ar units added to the C_{60} cage as indicated by FAB mass spectroscopy. The ^1H NMR spectrum indicates aromatic resonance (7.4 ppm) and a broad C-H peak (4.5 ppm) due to C_{60} skeletal hydrogens.^{22,31}

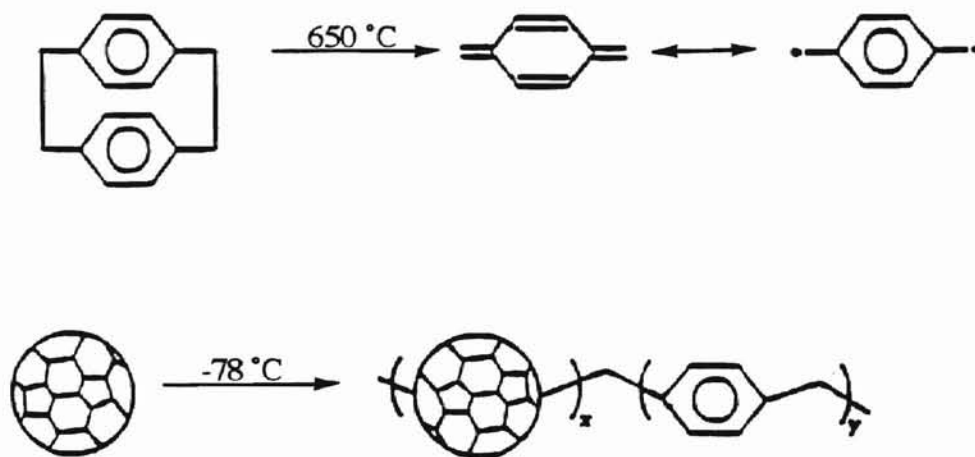
Scheme VI. Production of polyarenefullerenes.³¹



A free radical process has also been used to incorporate C_{60} into the polymer main chain.^{22,23,32} [2+2]-Paracyclophane was sublimed at 650 °C to form *p*-xylylene, a diradical analog of a benzyl radical, according to Scheme VII. The reaction produces a

copolymer at $-78\text{ }^{\circ}\text{C}$ that is insoluble in common organic solvents, which suggests crosslinking. Crosslinking was also indicated by thermogravimetric analysis (TGA). The ratio of C_{60} :xylylene was determined by elemental analysis to be 1.0:3.4, and the incorporation of C_{60} was determined by ^{13}C MAS NMR. Another problem with this reaction is that the product is unstable and readily reacts with oxygen.³²

Scheme VII. Formation of p-xylylene copolymers (x:y is 1.0:3.4).³²

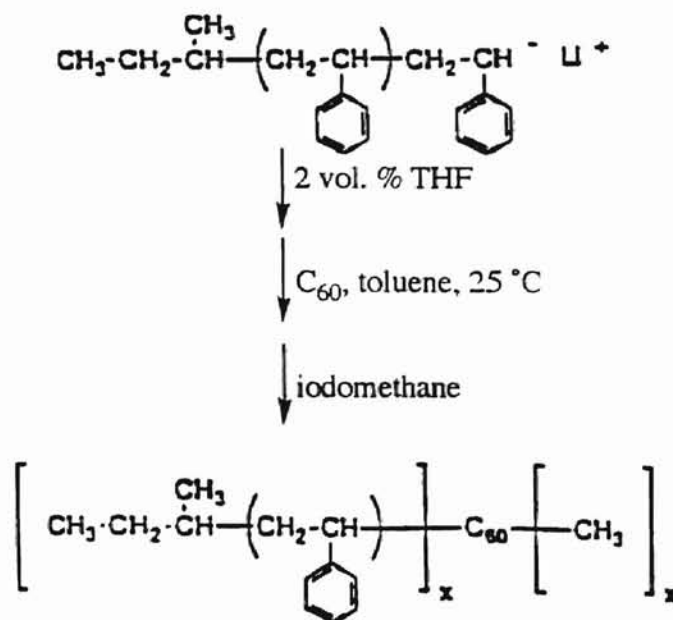


Recently, there have been two other examples reported for the preparation of C_{60} -polystyrene copolymers using a free radical polymerization.^{33,34} Azobisisobutyronitrile (AIBN) was used to initiate the reaction of C_{60} with styrene in bulk and in benzene solution. Soluble products with molecular weights of 14,400 for the solution polymerization and 256,000 for the bulk method were obtained.³³ The other example is similar except a benzoyl peroxide initiator was used, and toluene was the solvent. C_{60} was incorporated at 0.4% for the bulk procedure and 1.7% and 17% for the solution reactions. For each percentage of C_{60} , soluble products were obtained with molecular weights of 6.2×10^4 , 7.9×10^4 , and 1.7×10^4 respectively.³⁴ Both of these papers reported that the UV-Vis absorption spectra for the C_{60} -polystyrene copolymers are

strongly modified from the parent C_{60} . The characteristic C_{60} peaks were replaced by a structureless absorption pattern upon reaction with styrene.

Highly soluble and melt processable polymers can be made by reacting living polystyrene carbanion with C_{60} as shown in Scheme VIII.^{22,23,35} Gel permeation chromatography (GPC) results proved that the product consisted of a mixture of $C_{60}(PS)_x$ adducts with various polymer chain lengths and degree of substitution. The number of PS chains ranged from $x = 1$ to 10.³⁵

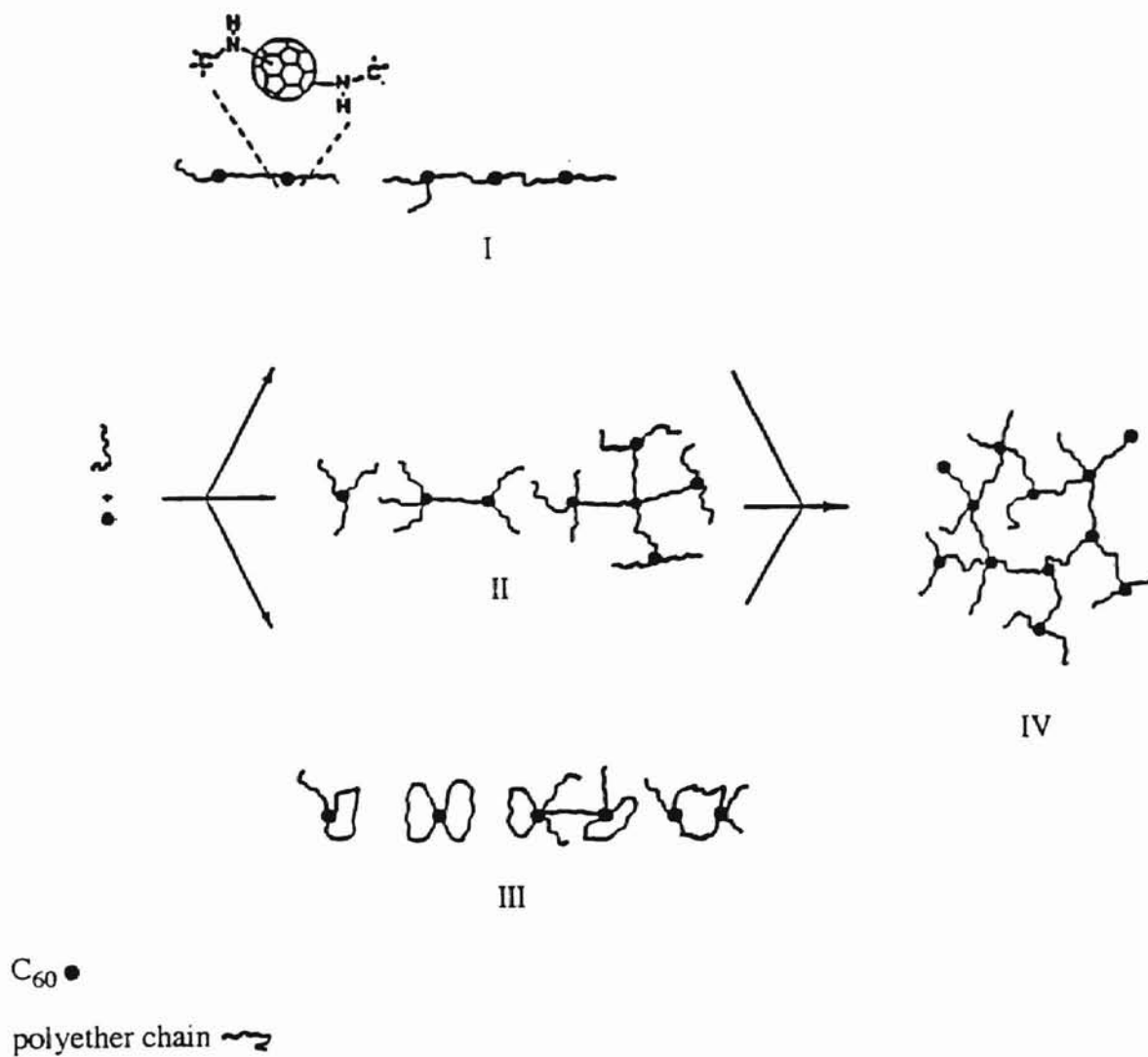
Scheme VIII. Living polymerization of polystyrene carbanion and C_{60} .³⁵



Amphiphilic derivatives of C_{60} are produced by the nucleophilic addition of bifunctional poly(oxyethylene) and poly(oxypropylene) with amino end-groups.³⁶ UV-Vis spectroscopy and GPC confirmed the interaction of C_{60} with the polyether. The molecular weights of the products range from 1400-3300 g/mol with an average of three polyether chains per C_{60} core. The ratio of polyether to C_{60} determines whether the

products will be soluble or not. With a 1:1 ratio, soluble products are formed either as linear, star-shaped, or branched derivatives as shown in Scheme IX. At 50:1 or 100:1, soluble products are only formed early in the reaction. At longer reaction times, the products may interact with each other or with unconsumed starting diamine to form crosslinked gels.^{23,36}

Scheme IX. Possible products formed by reaction of bifunctional polyethers and C_{60} .³⁶



Other examples include polymeric palladium-based materials $C_{60}Pd_n$ ^{22,23,37}, which exhibit catalytic activity in the hydrogenation of olefins and acetylene at room temperature; however, these are not polymers with long chains. C_{60} has been used as an initiator of polymerization for ethylene oxide and 1,3-butadiene.^{22,23,38} This method uses the stable and easily obtained $(C_{60})^{2+}$ for the initiation of sequential addition reactions.

Exposure of oxygen-free C_{60} films to light from a 300 W Hg arc lamp or an Ar-ion laser at 514.5 and 488.0 nm that exceeds $\approx 50 \text{ mW/mm}^2$ will polymerize C_{60} .^{22,23,42} After polymerization, the films are no longer soluble in toluene. From the IR- and Raman spectra, it was determined that C_{60} is linked together by C-C bonds. Laser desorption mass spectroscopy of the polymers showed up to 20 crosslinked C_{60} molecules. It has been suggested that a [2 + 2] cycloaddition occurred so as to convert the double bonds on adjacent molecules into a four membered ring (Figure 6).⁴² However, the results are only suggestive, and the exact nature of the mechanism and structure requires further research.

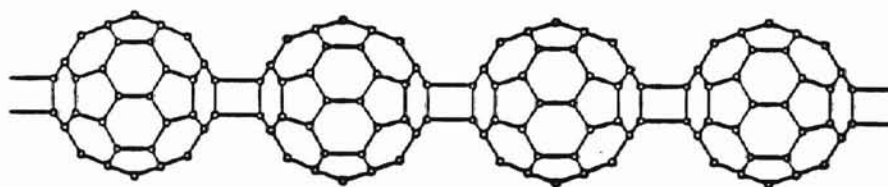
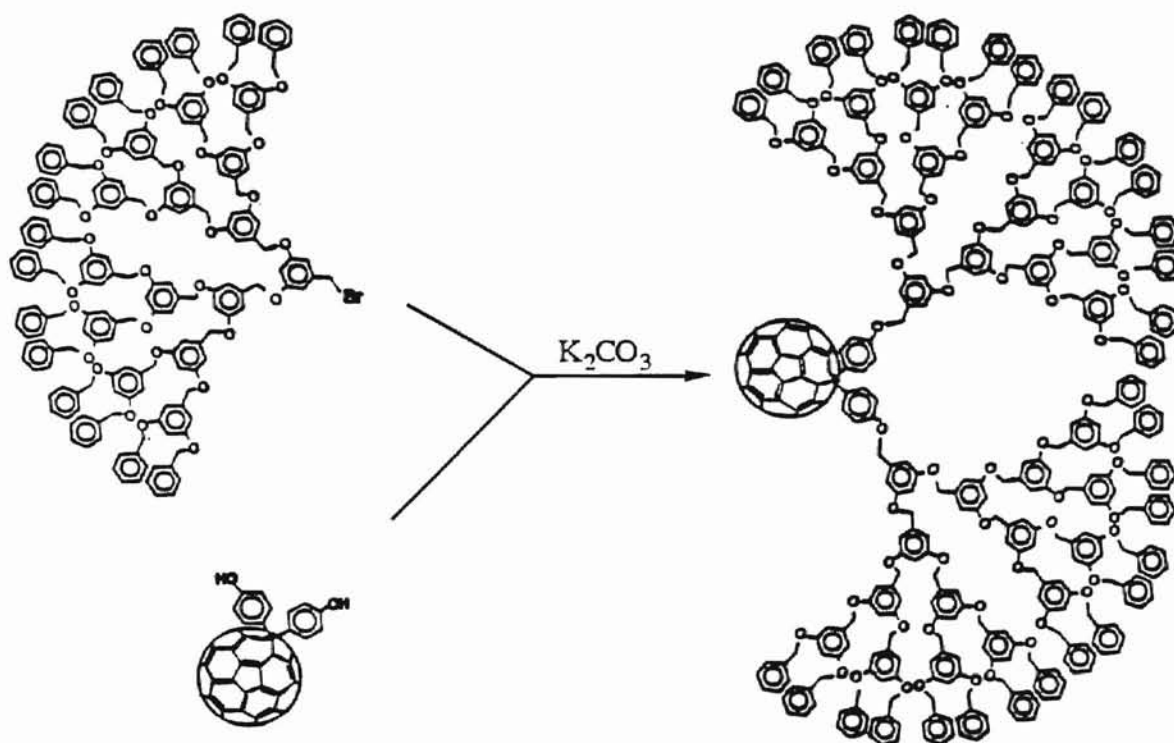


Figure 6. Photoinduced polymerization of C_{60} .⁴²

Scheme X shows the preparation of dendritic derivatives by reacting diphenolic fullerene with a fourth-generation dendrimer that contains a single benzylic bromide group.⁴³ SEC was used to monitor the coupling of the reactants, and ^{13}C NMR

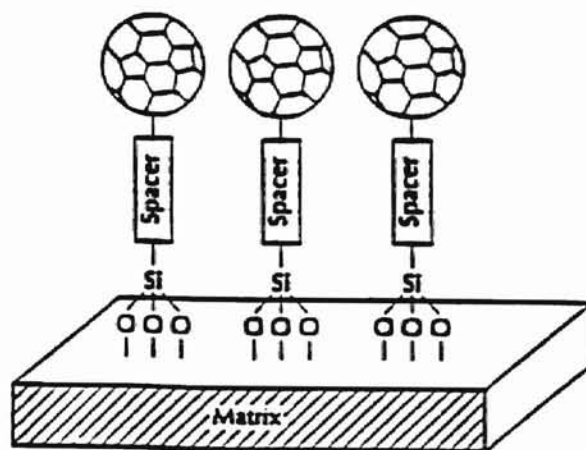
confirmed the covalent attachment. Alternatively, C_{60} can be directly reacted with dendritic azides.⁴⁴

Scheme X. Formation of dendritic derivatives.⁴³



Matrix-bound modification has been accomplished through two approaches. One is by functionalization of C_{60} in solution, and the other is by chemically modifying surfaces.²² An example of the second method is shown in Figure 7. Monolayered films of C_{60} are produced by reaction of terminal amino groups of organic-modified indium-tin oxide surfaces.^{22,39} These substrates were characterized by UV/Vis and cyclic voltametry. Similarly, C_{60} complexes with pyridyl terminated binding groups using quartz or Ge-Si as the substrates.^{22,40} Structural evidence was taken from X-ray diffraction data. The monolayers can be further functionalized by adding amine reagents to provide a route for growing three-dimensional structures.²² Wang has reported the use

of aluminum substrates for photoconducting films of polyvinylcarbazole doped with C_{60} .^{22,41}



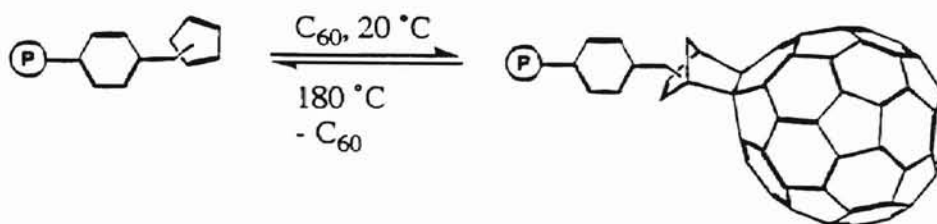
Preparation details for matrix-bound fullerenes

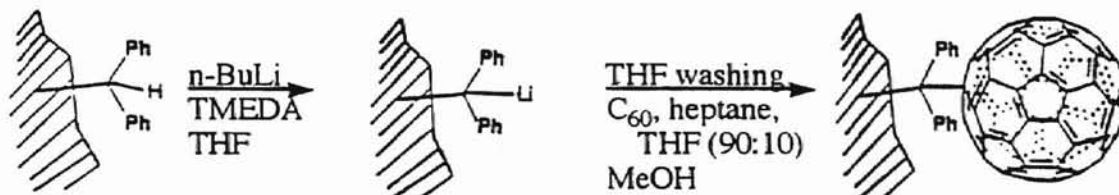
Matrix	Spacer group	Binding group
Indium-tin oxide	Trimethylene	NH
Quartz or Ge-Si multilayer	Undecane	Pyridyl-OsO ₄ complex

Figure 7. Illustration of matrix-bound C_{60} .²²

Two other examples of matrix-bound modification are the reversible addition of C_{60} to a polymer resin⁴⁵ and grafting C_{60} onto a polyethylene surface.^{22,23,46} Scheme XI shows the reaction of C_{60} with the cyclopentadiene-functionalized polymer support. The product is formed at room temperature, but it readily reverts back to the starting materials at temperatures greater than 95°C. Diphenylmethane-modified polyethylene films were deprotonated to give an anionic polyethylene surface which was used to covalently bind to C_{60} (Scheme XII).

Scheme XI. Covalent attachment of C_{60} to a polymer support.⁴⁵



Scheme XII. Grafting C_{60} onto polyethylene surface.⁴⁶

There have been many suggested uses for C_{60} derivatives along with several patent applications.⁴ Based on the known properties of C_{60} , it is believed that the polymeric products would possess remarkable electronic, optical, or catalytic properties.²² Macromolecular modification of C_{60} still remains in its infancy; however, as can be seen with the examples presented, there are many possible uses for these compounds. Some of these polymers might find applications in batteries, optical devices, chemical sensors, superconducting materials, additives, and biologically active compounds.²² It seems that the limiting factor for creating useful polymeric derivatives might only be one's imagination.

Objective of research. In the next chapter, the polymerization of C_{60} with styrene and methyl methacrylate will be discussed. The objective of this work has been to synthesize C_{60} polymers using different weight percents of C_{60} to determine how it affects the polymerization. Characterization of the products using conventional methods will also be discussed. The results indicate that new C_{60} polymers have been obtained. However, the percentage of C_{60} incorporated and the structure of the products have not been determined.

The long term objective is to incorporate C_{60} into latex particles via emulsion polymerization. Thin-films would then be made, and the third order nonlinear optical properties would be studied. However, C_{60} precipitates out during emulsion polymerizations because of its poor solubility. Therefore, polymeric derivatives were created using a free-radical polymerization. The derivatization improves the solubility so the functionalized C_{60} can eventually be used in an emulsion process.

CHAPTER II

EXPERIMENTAL

Materials. C₆₀ in >97% purity was obtained from Hoechst Celanese. Two different commercial batches were used for the experiments. C₆₀93 is from batch OP14/A, and C₆₀94 is from OP22. The o-dichlorobenzene (ODCB) and tetrahydrofuran (THF) were used as received. The methyl methacrylate and styrene monomer were distilled prior to use. Purities of both monomers were checked by ¹H NMR. The initiator, azobisisobutyronitrile (AIBN), had been recrystallized previously, and its purity was checked by NMR and FTIR.

Measurements. NMR spectra were recorded on a Varian-XL400 instrument. The FTIR spectra were recorded on a Nicolet Impact 400. Samples were either prepared as KBr pellets using air as the reference or as thin-films on NaCl plates. UV-Vis analyses were done using a Hewlett Packard 8452A diode array spectrophotometer. Quartz cells with path lengths of 1 cm were used. All gel permeation chromatography (GPC) analyses were performed with a Waters Model 590 pump using a Beckman 163 variable wavelength UV detector set at either 249 nm or 400 nm. Samples were analyzed with two 300 x 7.5 mm PLgel columns of 10⁵ and 10³ Å (10 μm) connected in series. Tetrahydrofuran (HPLC grade) was used as the mobile phase with a flow rate of 1 ml/min, and the chart speed was 0.5 cm/min. The calibration curve was constructed using polystyrene standards with the following number average molecular weights: 6.0 x 10⁵, 2.33 x 10⁵, 1.0 x 10⁵, 5.0 x 10⁴, 1.75 x 10⁴, 9.0 x 10³, and 2.0 x 10³. Molecular weight determinations were done by using Chromatochart-PC program from Interactive Microware, Inc. The mass spectral analyses of the samples were done by Dr. Dilip

Sensharma using the Liquid Secondary Ion Mass Spectrometry (LSIMS) technique. The instrument used was a VG Model ZAB2-SE mass spectrometer. The matrix used was *m*-nitrobenzyl alcohol. The Cs⁺ primary ion was set at 20 KeV.

Solution Preparation. The C₆₀ and AIBN samples were prepared in a dimly lit room by weighing the materials into separate vials which had been wrapped in aluminum foil. Using a syringe, the solvent (ODCB) was then added in the appropriate amounts. Samples were placed on an automatic shaker or in a sonicator to promote dissolution.

Reaction Procedures. Methyl methacrylate (MMA) reactions were carried out in test tubes which had been positioned in an oil bath and brought to a constant temperature of 70 °C. Methyl methacrylate was weighed in a vial and transferred into the reaction vessel. After the test tubes were allowed to equilibrate in the oil bath, C₆₀ solutions were added to the appropriate test tubes followed by the addition of the initiator 15 minutes later to all reaction vessels. The mixtures appeared to be homogeneous. The reactions were allowed to go for a minimum of 17 hours before being brought to room temperature. The reactions involving only C₆₀ and AIBN were carried out using the above conditions.

The styrene reactions were carried out in a 25 or 50 ml, 3-neck round bottom flask which was fixed in an oil bath that had been heated to a constant temperature of 64 °C. The reaction flask was equipped with a nitrogen inlet, a condenser, and a mechanical stirrer. The monomer was weighed in a vial and transferred into the reaction vessel. After equilibration of the monomer, C₆₀ solution was then transferred. Nitrogen was bubbled through the solutions while being stirred for at least 15 minutes before adding the initiator. After a minimum of 16 hours, the reactions were stopped and brought to room temperature. Solutions appeared to be homogeneous. The amount of C₆₀ used in a reaction was 1, 5, or 10 wt.% relative to the monomer. The molar ratio of C₆₀:AIBN was 1:5 for all polymerization reactions. Table II provides the amounts of starting materials used for each reaction.

Table II. Starting materials for polymerization of C₆₀ and control reactions.

Sample ID	Monomer (g)	AIBN (mg)	C ₆₀ (mg)	ODCB (ml)	Recovery (g)	% Yield	Product Description
1%-PMMA	2.4360	33.2	24.4 ^a	5	1.648	67.0	light brown powder
1%-PMMA control	2.4330	29.2		5	1.940	79.7	white chunks
5%-PMMA	2.5010	142.8	125.0 ^a	8	1.694	64.5	dark brown chunks
5%-PMMA control	2.5080	142.9		8	2.055	81.9	white chunks
10%-PMMA	2.5050	285.2	250.2 ^a	16	0.138	5.0	dark brown fine solids
10%-PMMA control	2.5000	284.9		16	1.434	57.4	white chunks
C ₆₀ :AIBN (1:5)		37.5	30.9 ^b	4	0.055	80.4 ^c	black fine solids
C ₆₀ :AIBN (5:1)		7.7	161.7 ^b	7	0.109	64.3 ^c	black fine solid
1%-PS	2.4418	27.8	24.5 ^a	5	0.143	5.7	light brown chunks
1%-PS control	2.4659	28.8		5	0.811	32.5	white chunks
5%-PS	2.5130	147.9	128.8 ^b	8	0.175	6.3	black fine solid
5%-PS control	2.5170	147.1		8	1.045	39.2	white chunks
10%-PS	2.5100	292.9	258.6 ^b	16	0.250	8.2	black fine solid
10%-PS control	2.501	296.2		16	0.102	3.6	white fine solids

^a C₆₀ was taken from commercial batch Op 14/a. ^b C₆₀ was taken from commercial batch Op 22. ^c Reported as percentage of C₆₀ and AIBN.

Workup Procedure. The polymethylmethacrylate (PMMA) and polystyrene (PS) samples were treated in the following manner. The reaction mixture was added dropwise into a ten-fold excess of magnetically stirred diethyl ether or methanol, at which point the product(s) precipitated immediately. The 1% PMMA and PS samples were vacuum filtered onto a medium or coarse sintered glass funnel and washed with ether or methanol. Next, they were dissolved in either acetone or chloroform, reprecipitated into methanol, filtered, and dried overnight in a vacuum desiccator at 80 °C.

The 5 and 10% samples of PMMA and PS were centrifuged after precipitation of the product. After the mother liquor was decanted, the precipitate was washed with methanol, sonicated, centrifuged, and decanted again. Finally, the precipitate was dried at 80 °C in a vacuum desiccator. Products were precipitated and washed only one time.

The C₆₀:AIBN reaction mixtures which contained no polymer, were diluted with 15-20 ml methanol, transferred to a round bottom flask and rotary evaporated. This process was repeated several times. The resulting brown pasty liquid was dried overnight in the vacuum desiccator at 80 °C. Note: the 5:1 sample had some black solids remaining in the test tube when the liquid was transferred to a round bottom flask despite the reaction mixture looking homogeneous. A brief description of every reaction mixture is given in Table II.

RESULTS

The amounts of material recovered and the percent yield from each reaction are reported in Table II.

FTIR Analyses. The first spectrum appearing in Figure 8 is of pure C_{60} . Due to its truncated icosahedral symmetry, it has four IR active bands located at 527, 576, 1183, and 1429 cm^{-1} . Figure 9 is of the C_{60} :AIBN (1:5) sample. None of the four C_{60} peaks are present. The spectrum shows $-CH_3$ bending (1466, 1368, 1455 cm^{-1}), C-C double bond stretching (1630 cm^{-1}), $-C-H$ stretching (2800- 2990 cm^{-1}), and $-CN$ group (2220 cm^{-1}). The peaks around 755, 1035, and 1160 cm^{-1} may be due to ODCB or AIBN fragments. The FTIR spectra of KBr, AIBN, and ODCB have been included for reference in Figures 10-12. The FTIR spectrum (Figure 13) for the 5:1 sample shows all the major C_{60} peaks at 527, 576, 1183, and 1430 cm^{-1} which is to be expected since the amount of C_{60} is much greater than the initiator. There are a few other minor peaks close to the baseline which coincide with peaks in the 1:5 sample.

The FTIR analyses does not provide any distinction between the three C_{60} -PMMA polymer samples, and there is no identification of any C_{60} peaks. Each sample shows the carbonyl (1730 cm^{-1}), $-C-H$ stretching (2850-3000 cm^{-1}), $-C-H$ bending (1450-1490 cm^{-1}), C-O bending (1145, 1195 cm^{-1}), and the peaks in the 1200 cm^{-1} region have not been assigned. Figures 14-16 provide the spectra of the C_{60} -PMMA samples. The spectra of the control samples are consistent with the spectra of samples containing C_{60} .

The FTIR spectrum of C_{60} (1%)-PS product (Figure 17) shows the monosubstitution pattern of polystyrene (695, 755 cm^{-1}), $-C-H$ stretching (2852, 2924 cm^{-1}), Ar-H stretching (3024 cm^{-1}), and the characteristic polystyrene peak (1601 cm^{-1}). There are no apparent differences between this sample and its control. The FTIR analyses of C_{60} (5%)- and C_{60} (10%)-PS samples were attempted without success. Both of these samples are partially insoluble in THF, which causes diffraction problems. When the samples were filtered, they were not concentrated enough to obtain an adequate spectrum.

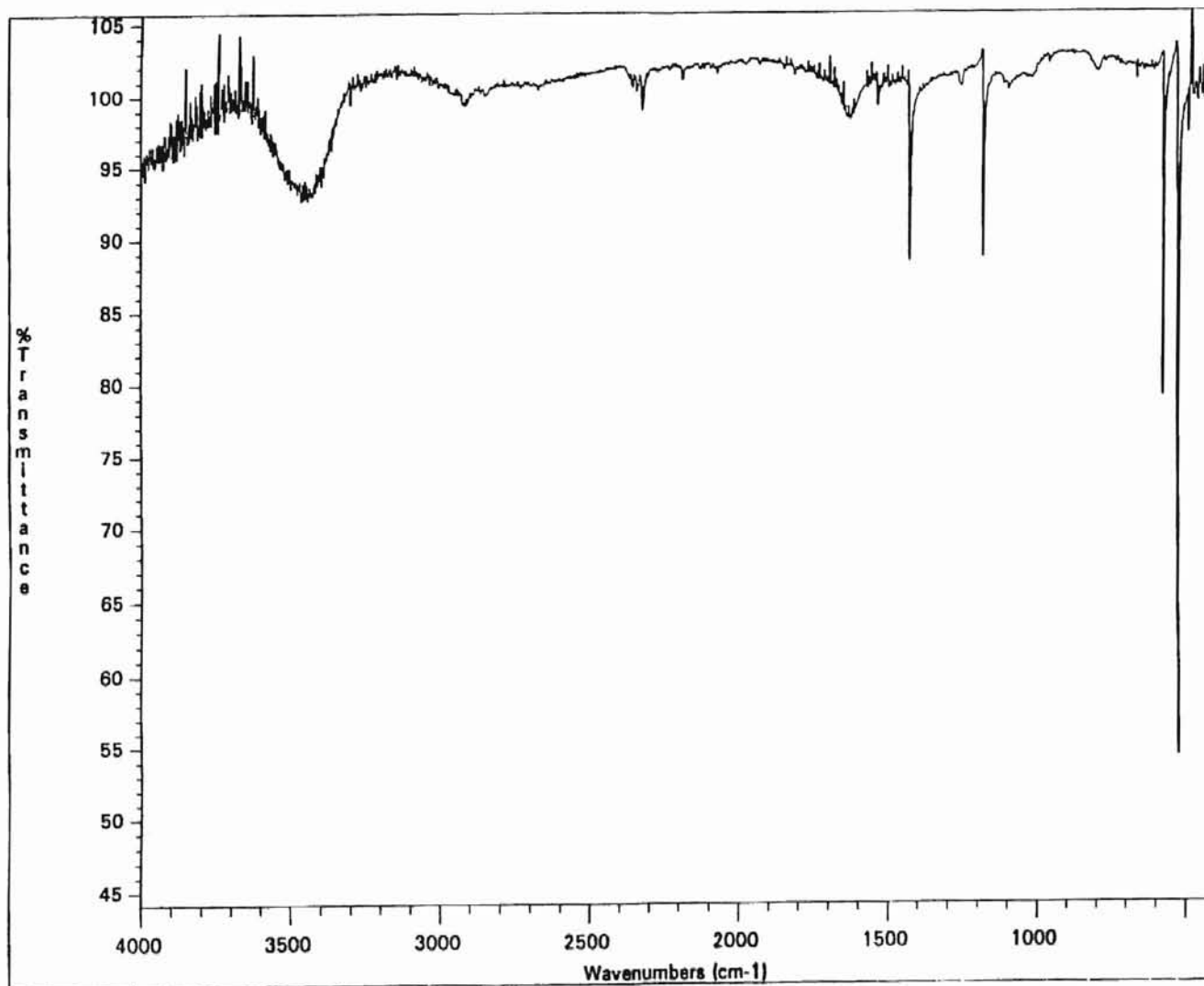


Figure 8. FTIR Spectrum of C₆₀ (KBr pellet).

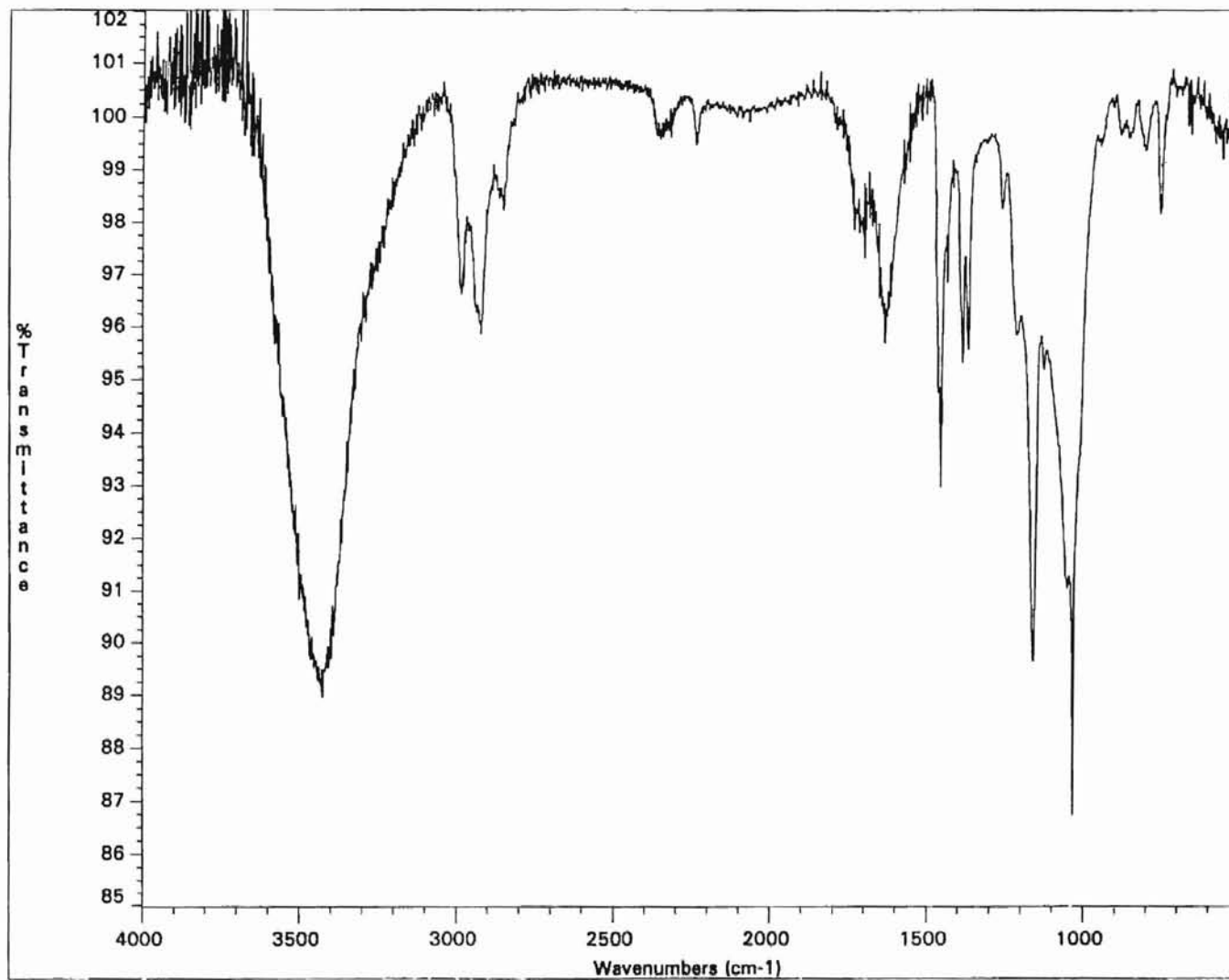


Figure 9. FTIR Spectrum of C₆₀:AIBN (1:5) (KBr pellet).

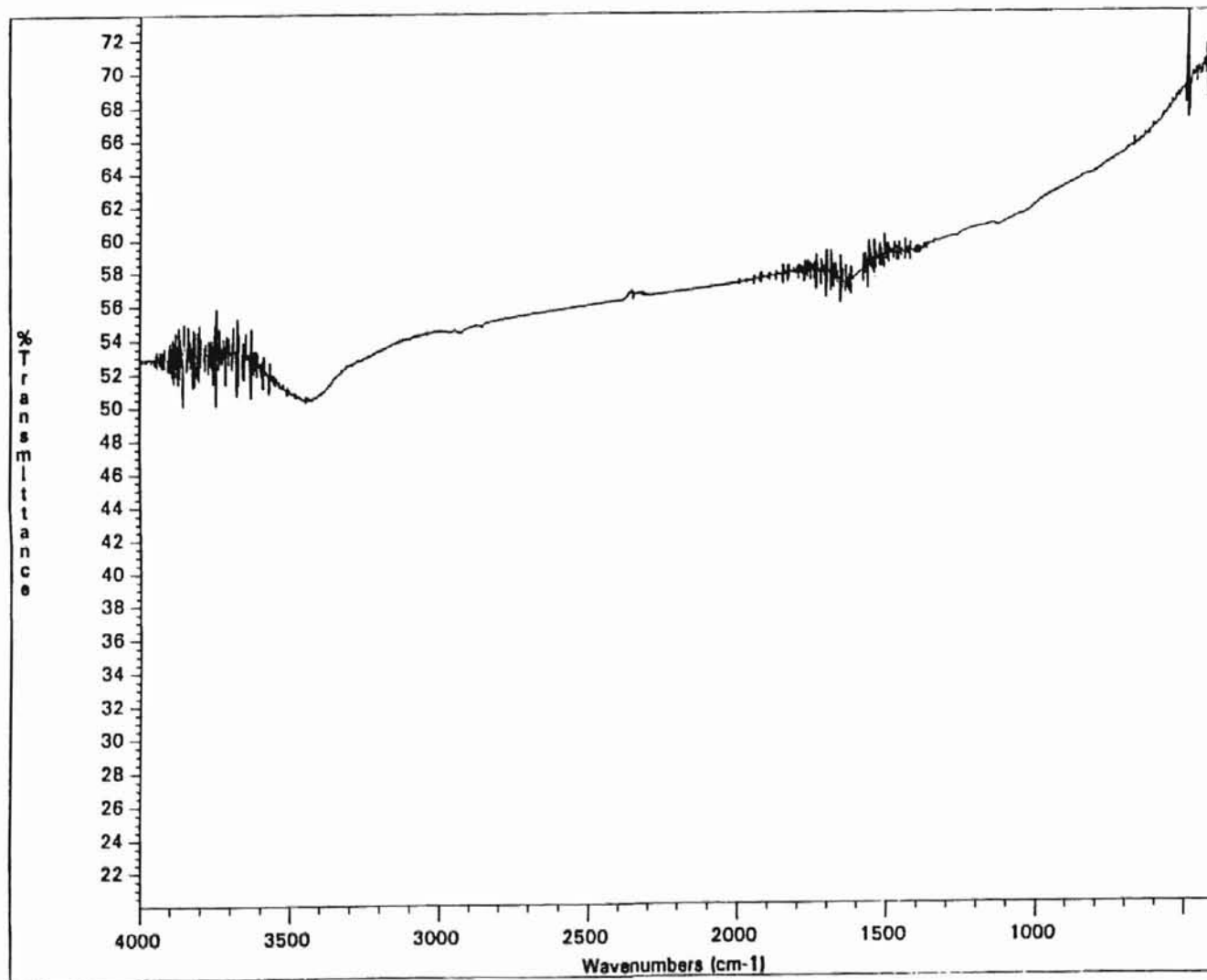


Figure 10. FTIR Spectrum of KBr pellet.

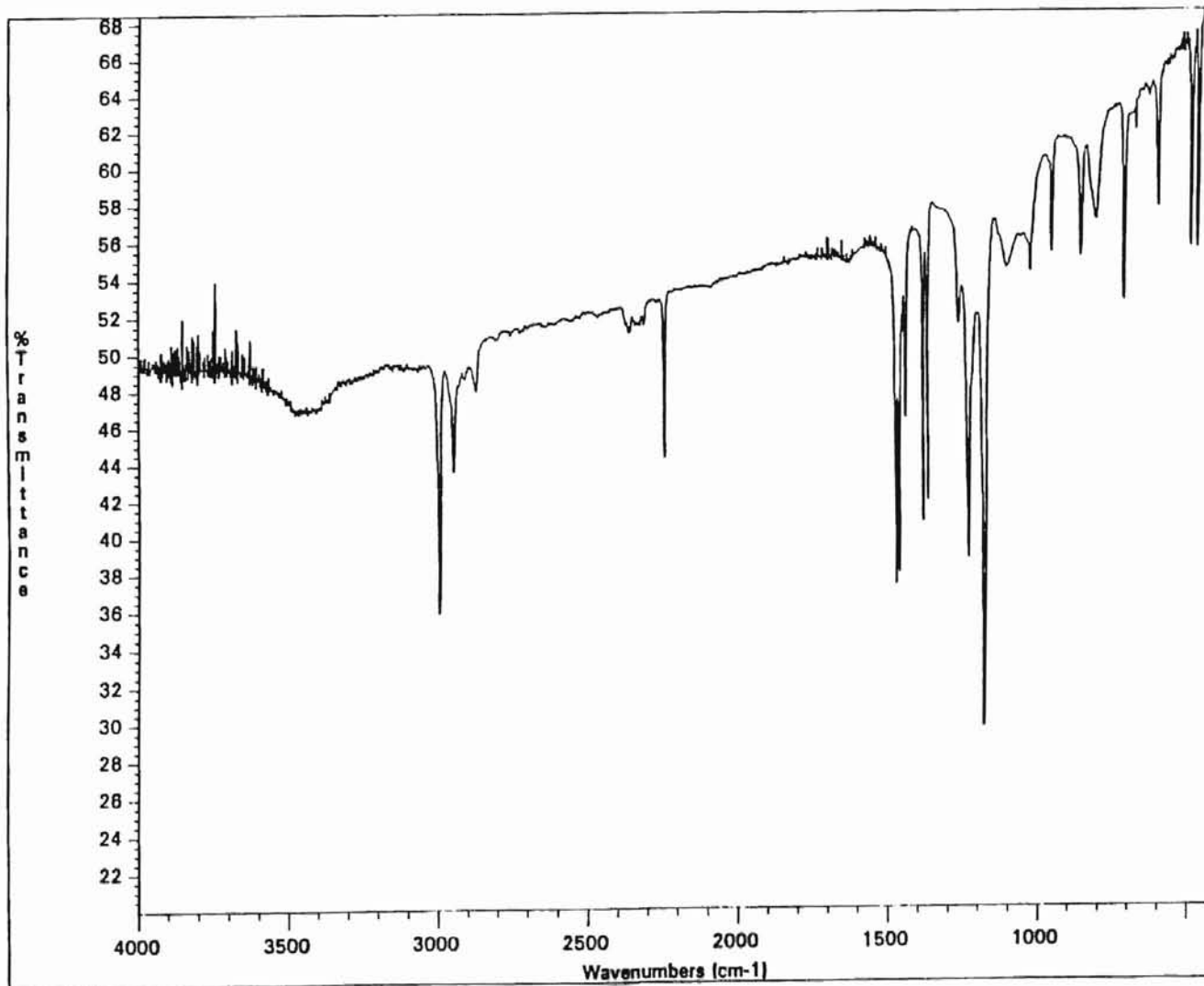


Figure 11. FTIR Spectrum of AIBN (KBr pellet).

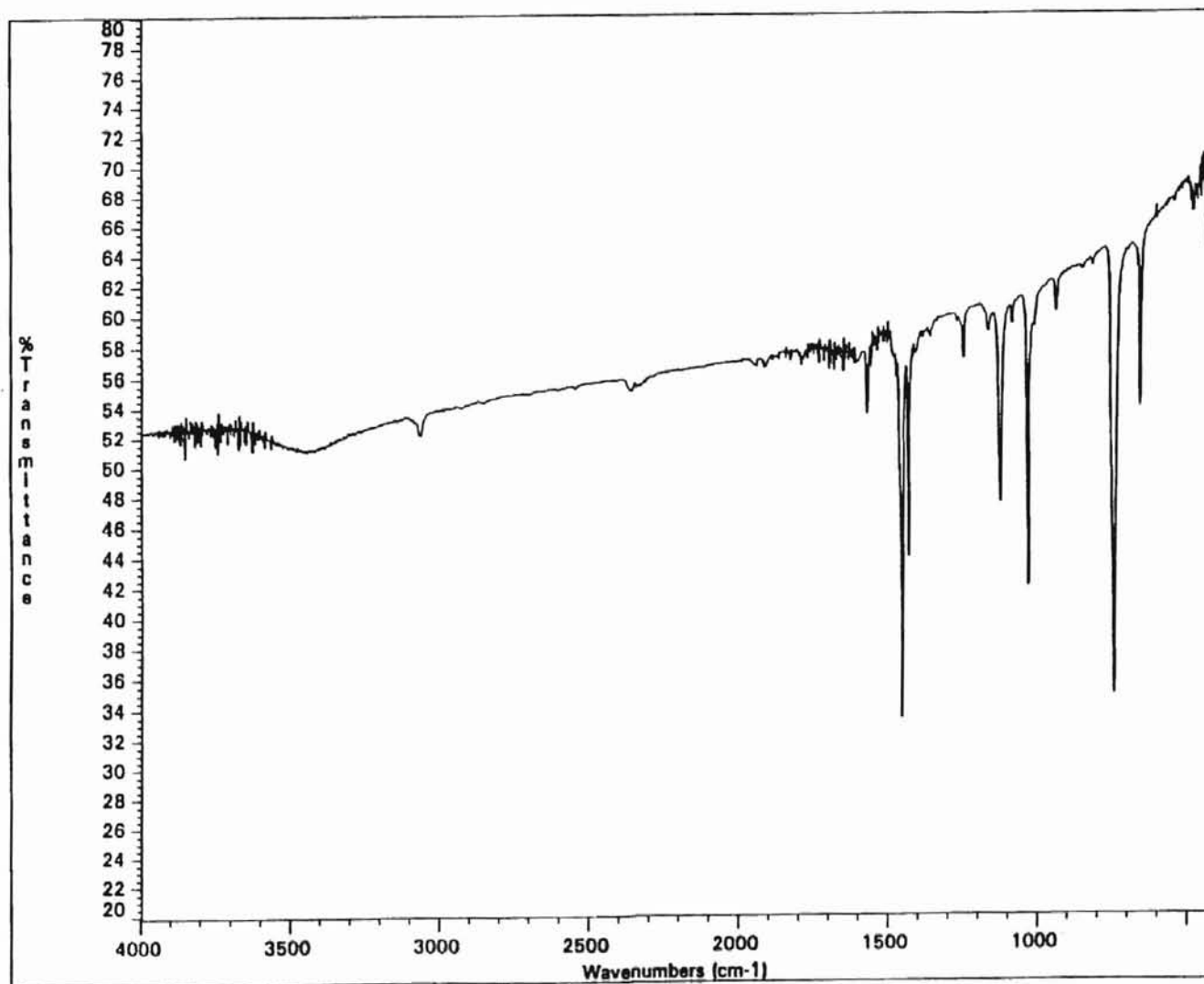


Figure 12. FTIR Spectrum of o-dichlorobenzene (neat).

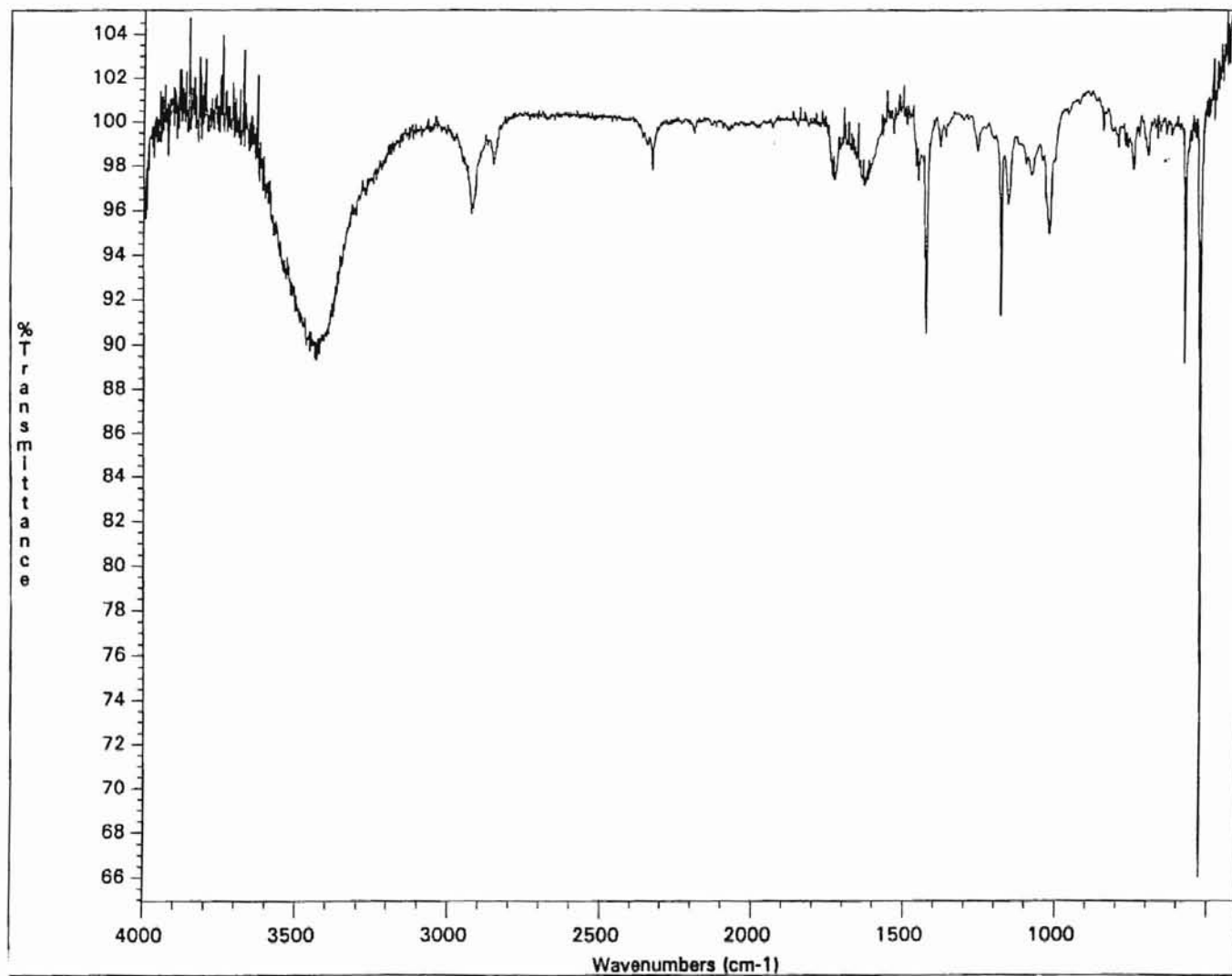


Figure 13. FTIR Spectrum of C₆₀:AIBN (5:1) (KBr pellet).

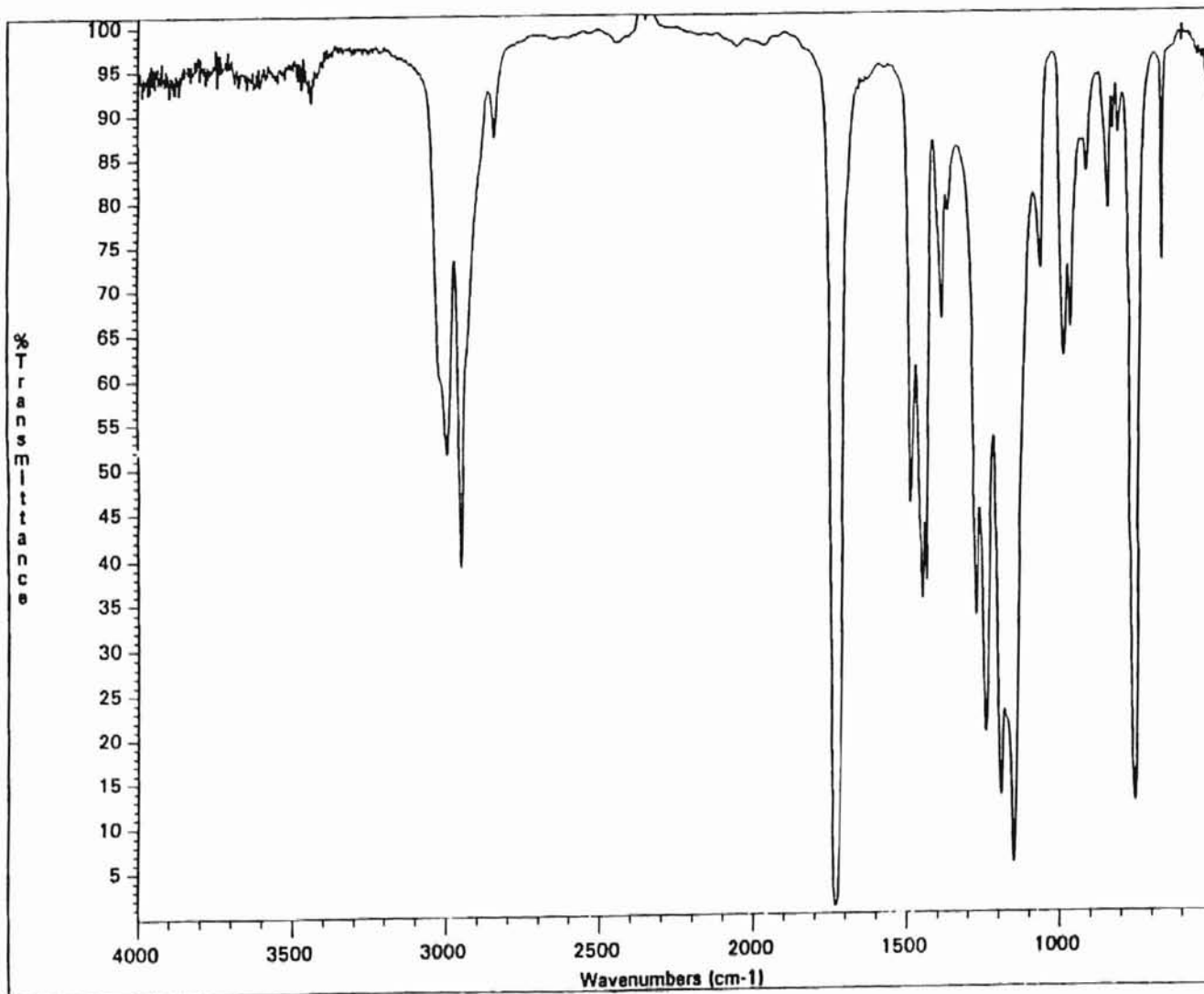


Figure 14. FTIR Spectrum of C₆₀(1%)-PMMA (KBr pellet).

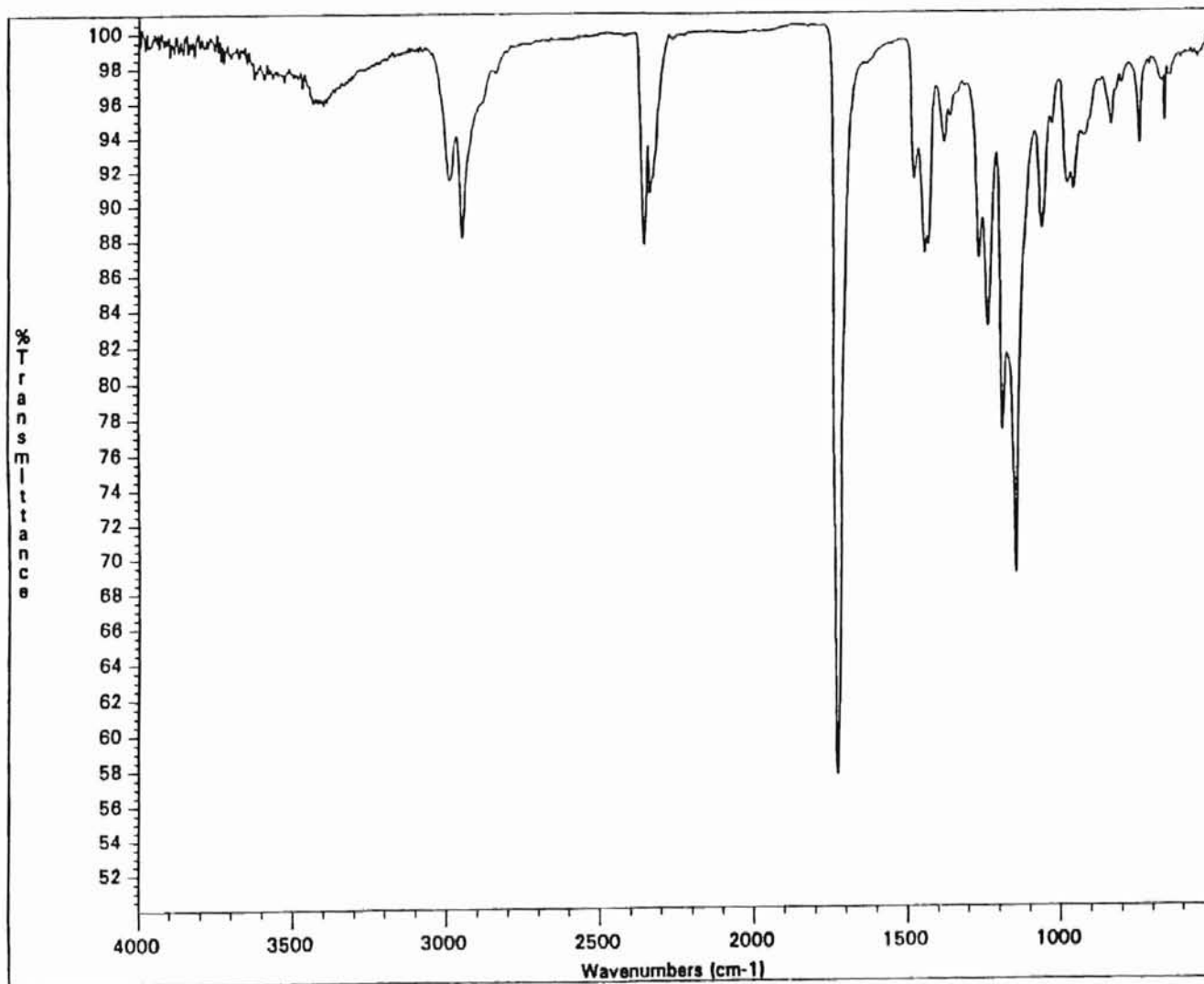


Figure 15. FTIR Spectrum of C₆₀(5%)-PMMA (KBr pellet).

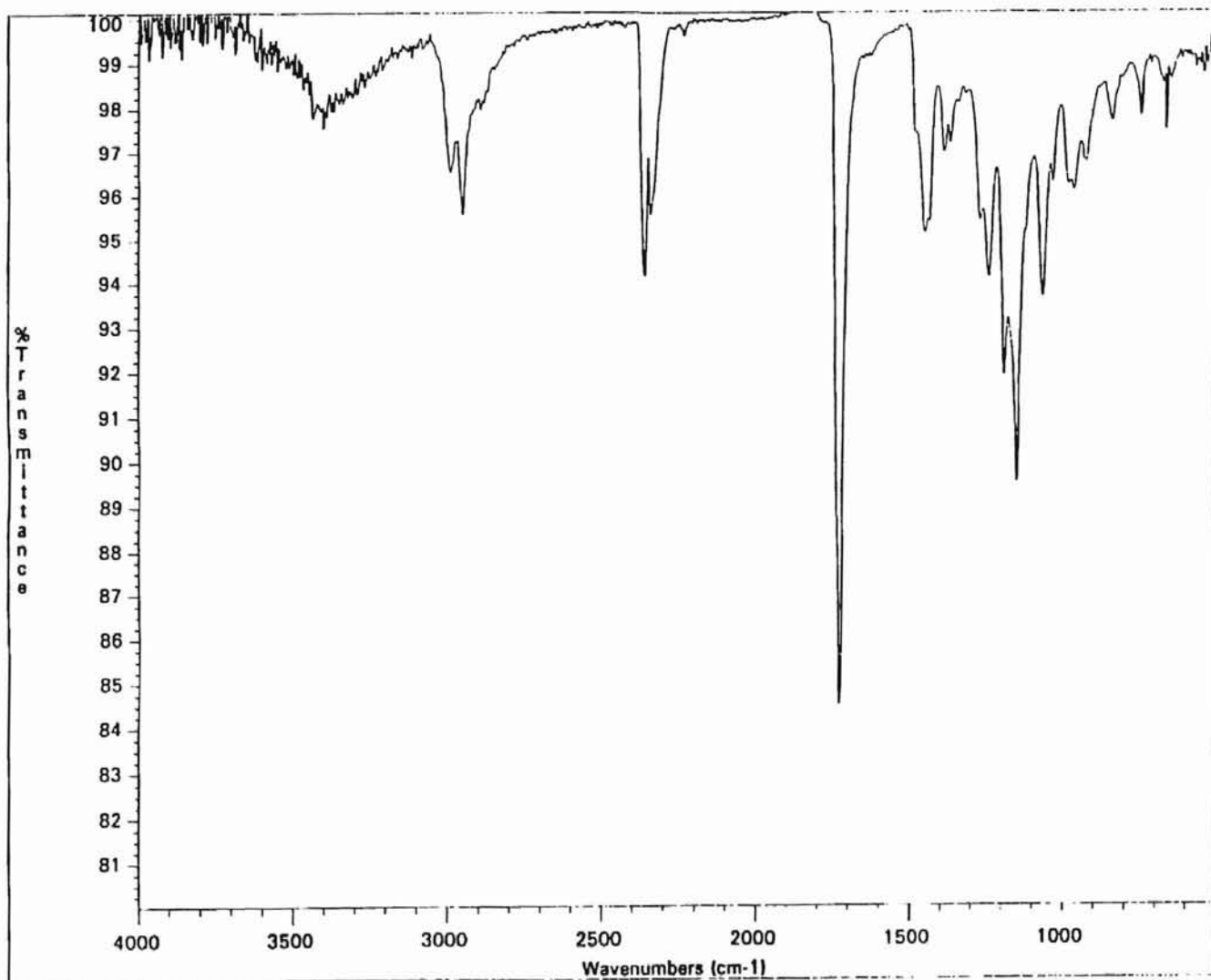


Figure 16. FTIR Spectrum of C₆₀(10%)-PMMA (KBr pellet).

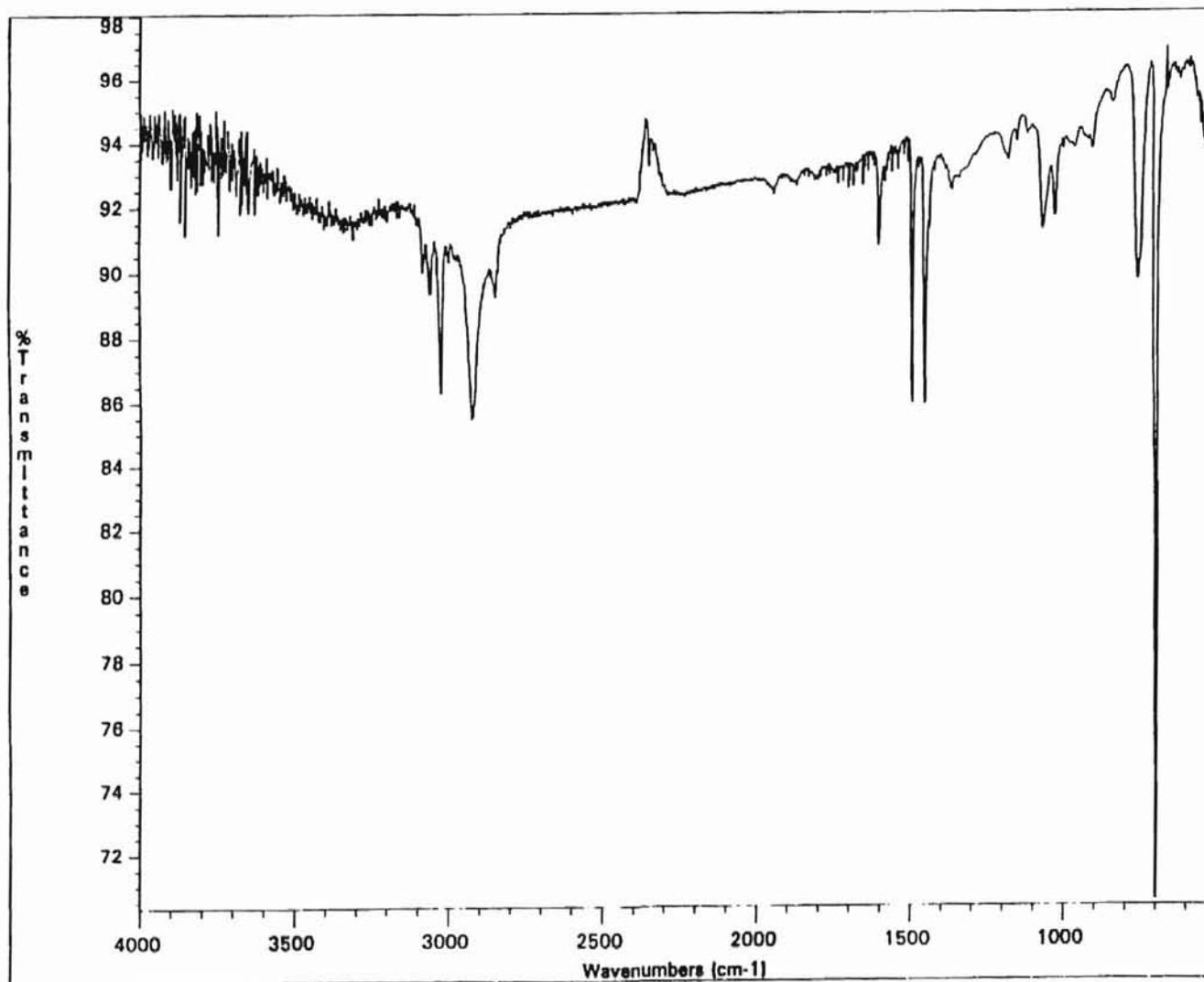


Figure 17. FTIR Spectrum of C₆₀(1%)-PS (KBr pellet).

Mass Spectroscopic Analyses. In Figure 18, the FAB mass spectrum of C₆₀:AIBN (1:5) shows a peak at every 24 mass units beginning with m/z 528. This 24 mass units could only be two carbon units. At this time, it is not known if the series of peaks are due to the spectroscopic method breaking the spherical cage or if the C₆₀ is opened during the chemical reaction. Also, the series of peaks could be due to a series of compounds. The sample shows peaks up to m/z 2600 which suggest one to three C₆₀ molecules with the remaining mass attributed to AIBN components. The sample C₆₀:AIBN (5:1) does not show as high of a molecular weight and only a short series of peaks was found from 648 to 840 amu (Figure 19).

UV-Visible Analyses. The UV-Vis spectra for both C₆₀ commercial samples were taken in THF. They each show λ_{max} at 216, 258, and 330 nm. However, C₆₀93 has a 406 nm peak and C₆₀94 has a peak at 404 nm. They both show a tailing absorption out to 800 nm. C₆₀ is not completely soluble in THF; therefore, the extinction coefficients could not be calculated. Figure 20 contains the spectrum for C₆₀93. The spectrum for C₆₀:AIBN (1:5) (Figure 21) has an absorption maximum near 220 nm and a tail that extends out past 500 nm. The disappearance of the distinct peaks in the absorption spectrum of C₆₀ is characteristic of the spectra of many C₆₀ derivatives. This sample was completely soluble in THF which also indicates that it has been derivatized.

The C₆₀:AIBN (5:1) spectrum is significantly different from the 1:5 sample. It has absorption peaks at 404, 330, 258, and around 220 nm. The sample also has solubility problems in THF. The partially dissolved sample was analyzed, filtered, and re-examined. After filtering the solution and redoing the analysis, the spectra look the same. Although, the filtered solution does show decreased absorption as one would expect, and the 404 peak now appears at 406 nm. Figure 22 shows the C₆₀:AIBN (5:1) spectrum of

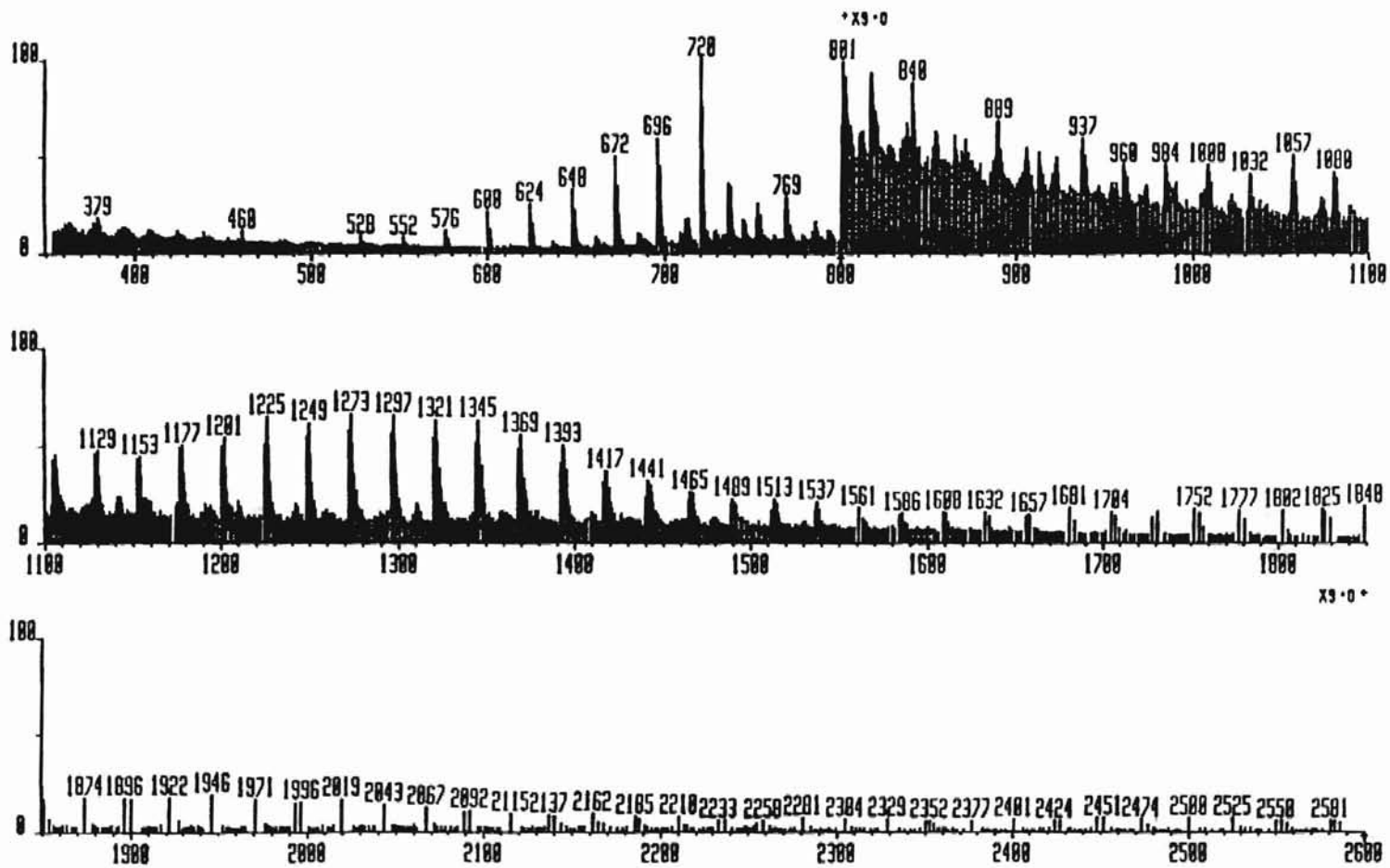


Figure 18. FAB Mass Spectrum of C₆₀:AIBN (1:5).

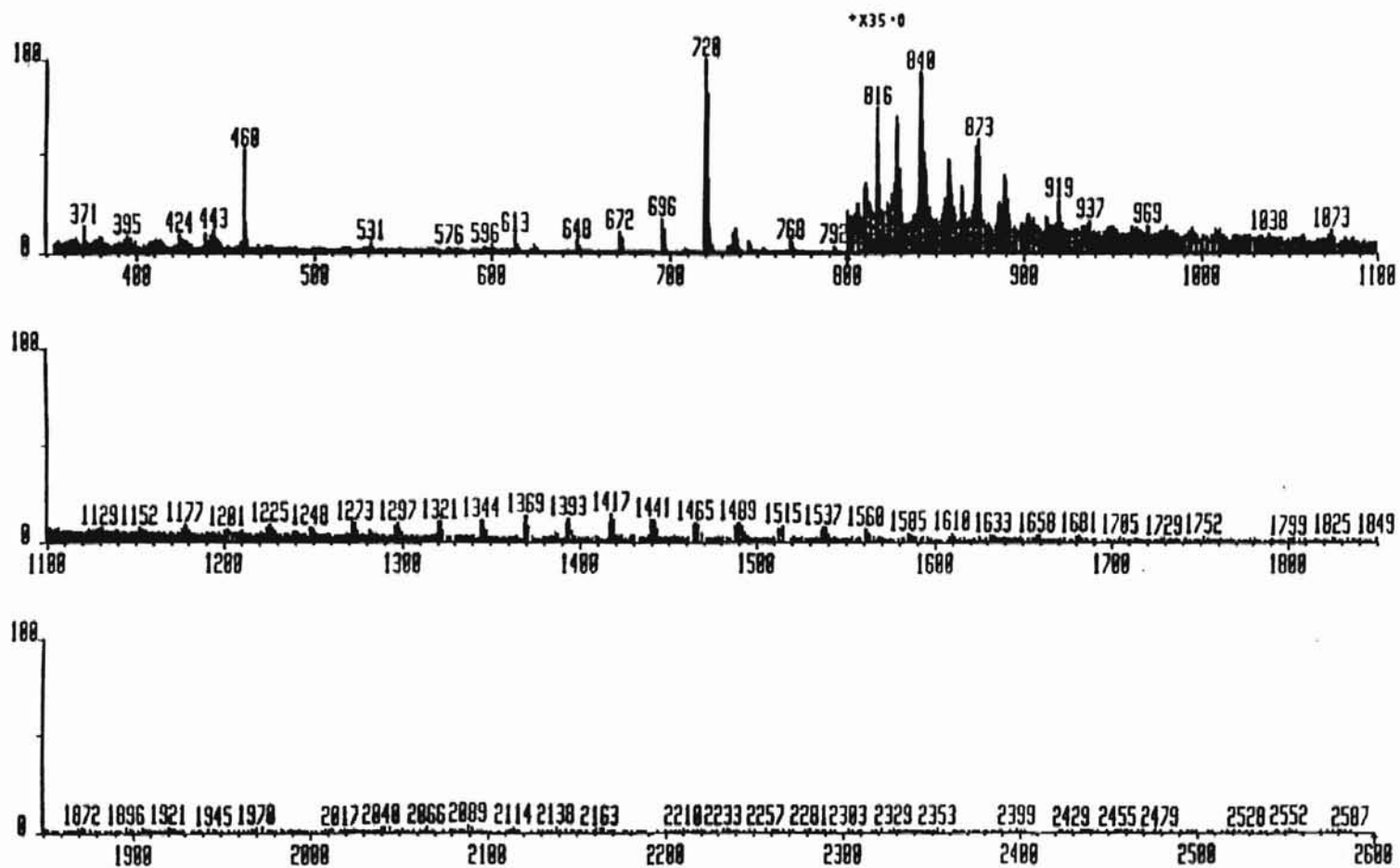


Figure 19. FAB Mass Spectrum of C₆₀:AIBN (5:1).

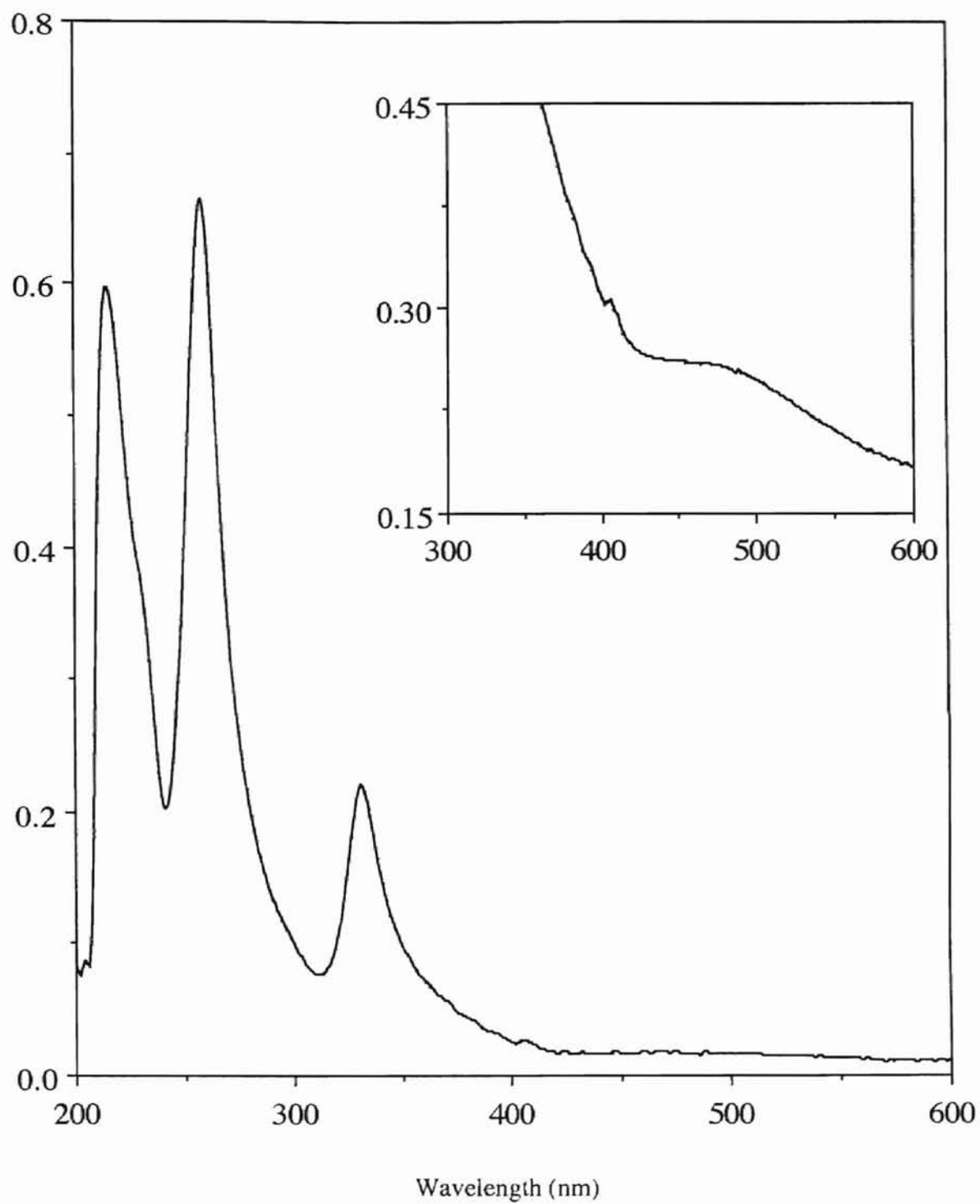


Figure 20. UV-Visible Spectrum of C₆₀.

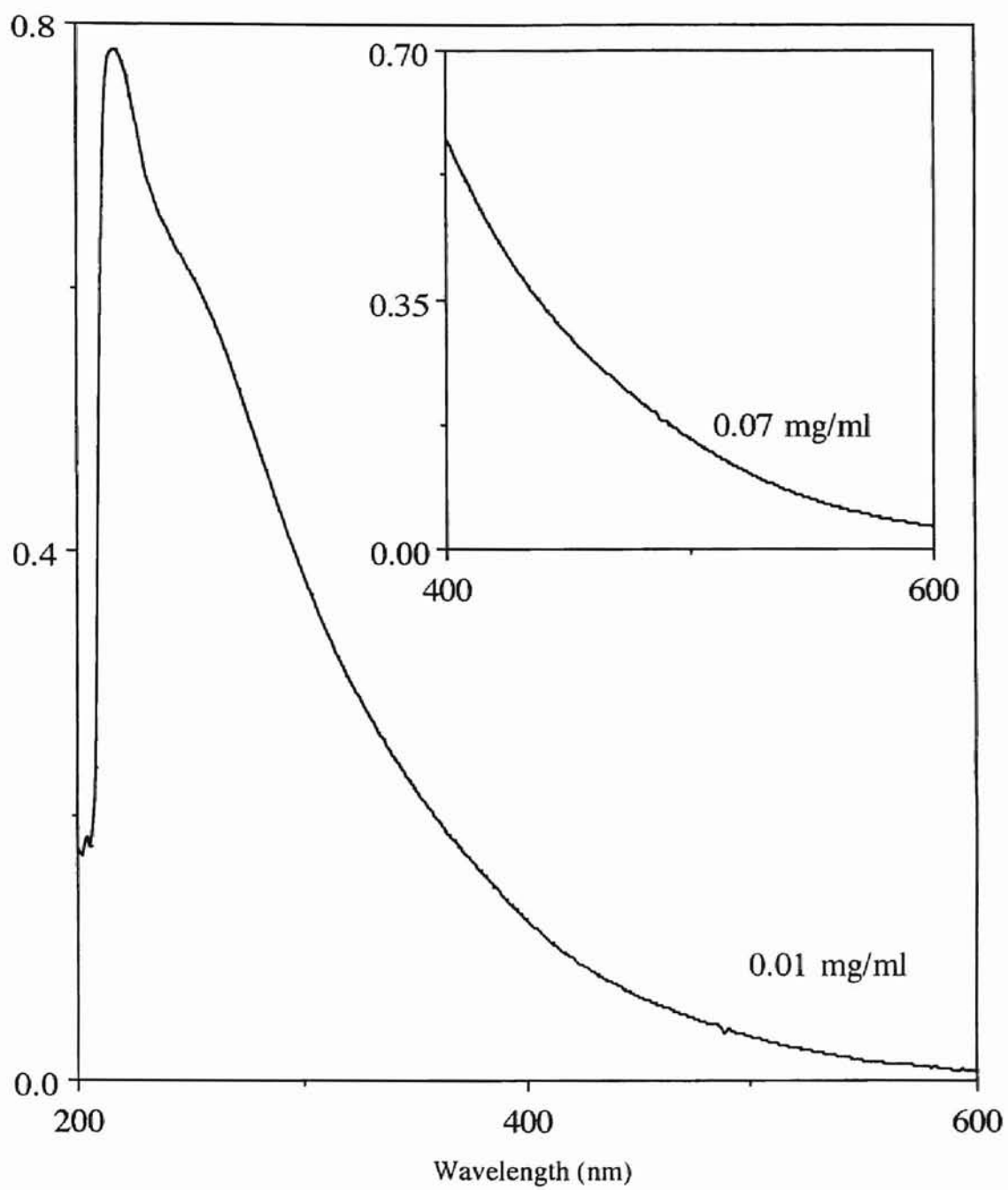


Figure 21. UV-Visible Spectrum of C₆₀:AIBN (1:5).

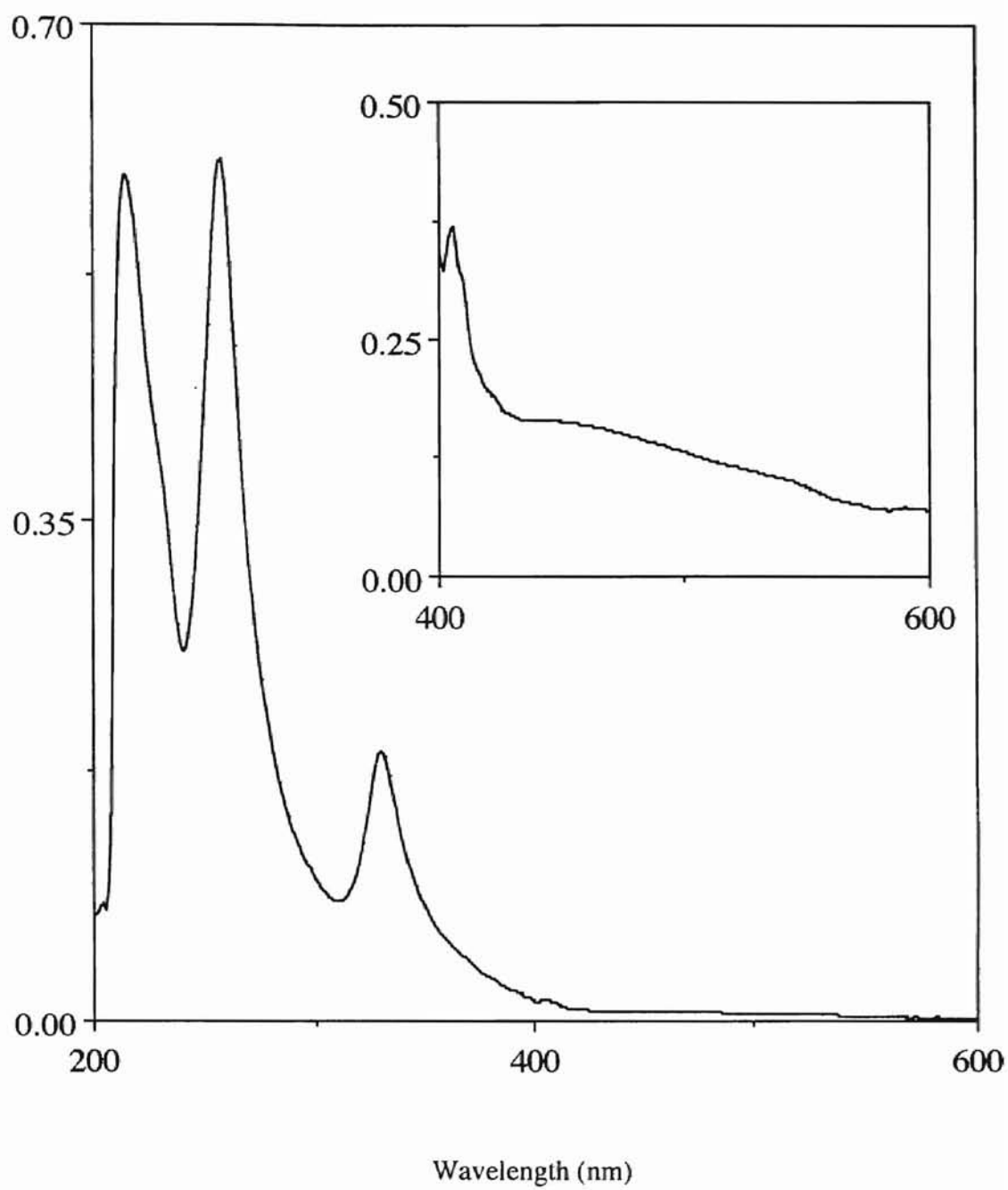


Figure 22. UV-Visible Spectrum of C₆₀:AIBN (5:1).

the filtered solution. These results support the presence of underivatized C₆₀, which is also indicated by the FTIR spectrum.

Analysis of the C₆₀(1%)-PS has a maximum absorption in the 220 nm region followed by a sharp drop and a tailing absorption out to 600 nm (Figure 23). This spectrum looks much like commercial polystyrene. The most notable difference is polystyrene does not absorb past 300 nm, whereas, this 1% sample does. The C₆₀(5%)-PS sample did not completely dissolve in THF, thus, showing more C₆₀ like character. It has a λ_{max} near 220 nm, but there is no immediate drop in absorption. In Figure 24, the absorption tails out past 600 nm, and there are small shoulders where C₆₀ peaks occur. The spectrum for the 10% C₆₀ sample (Figure 25) shows maximum absorptions which are close to the reported absorbances of C₆₀. Furthermore, the 10% sample was not completely soluble in THF.

The UV-Visible spectrum (Figure 26) for the C₆₀(1%)-PMMA polymer sample shows λ_{max} near 220 nm followed by the tailing absorption that is comparable with the spectrum of the 1% PS derivative. Unlike the 1% PS sample, the incorporation of C₆₀ is more readily seen by the small shoulders appearing around 260 and 330 nm. PMMA should not show any absorption itself; therefore, one might conclude that the absorption seen in Figure 26 is due to only C₆₀. However, the presence of o-dichlorobenzene can not be ruled out. The C₆₀(5%)-PMMA spectrum in Figure 27 has a maximum absorption with broad tailing much like the 1% PMMA spectrum. Interestingly, the spectrum in Figure 28 for 10% PMMA sample is nothing like the 10% PS spectrum; there are no distinct C₆₀ peaks. All of the PMMA samples were readily soluble in THF. Table III provides absorptivity values for each soluble sample.

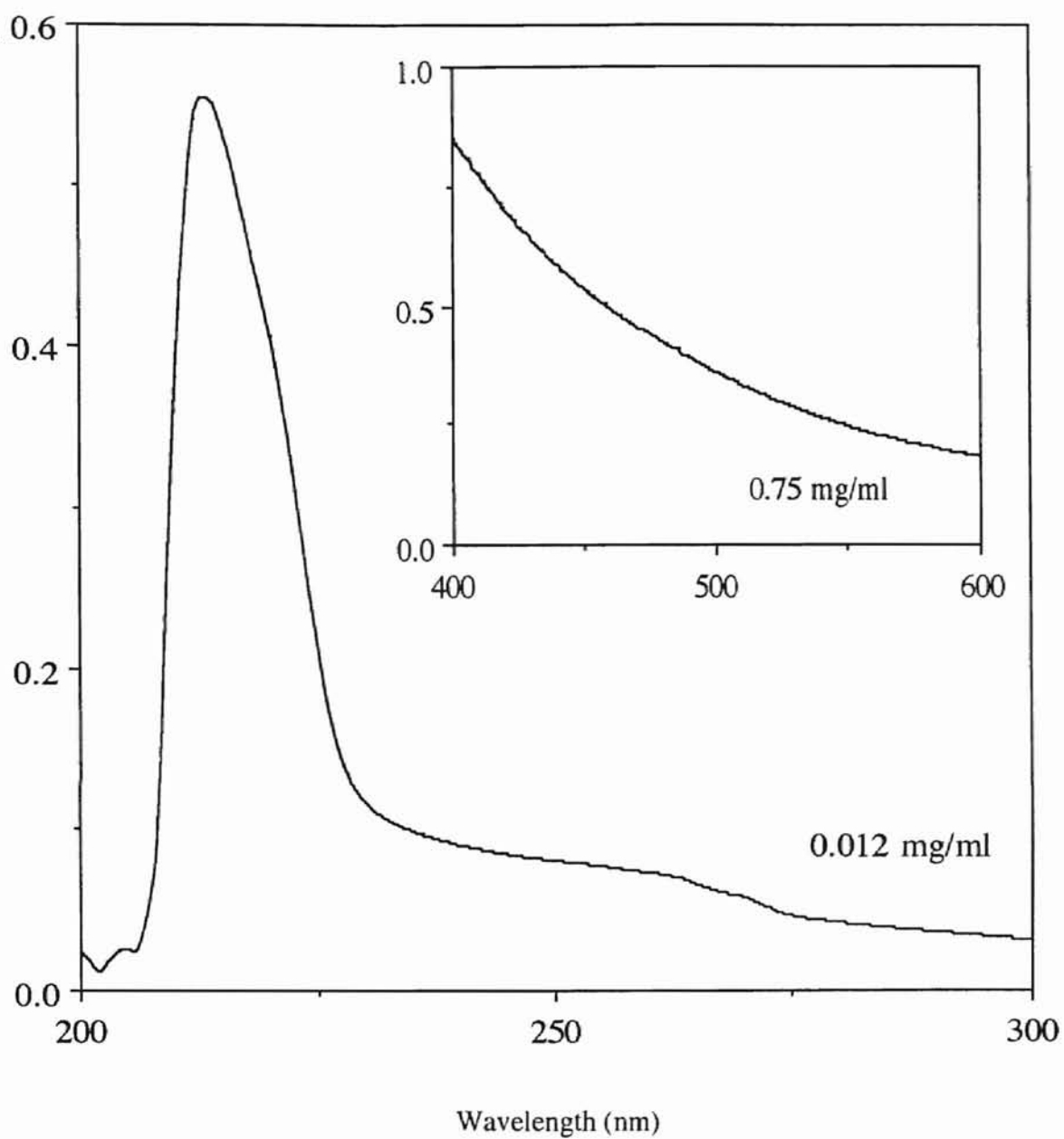


Figure 23. UV-Visible Spectrum of C₆₀(1%)-PS.

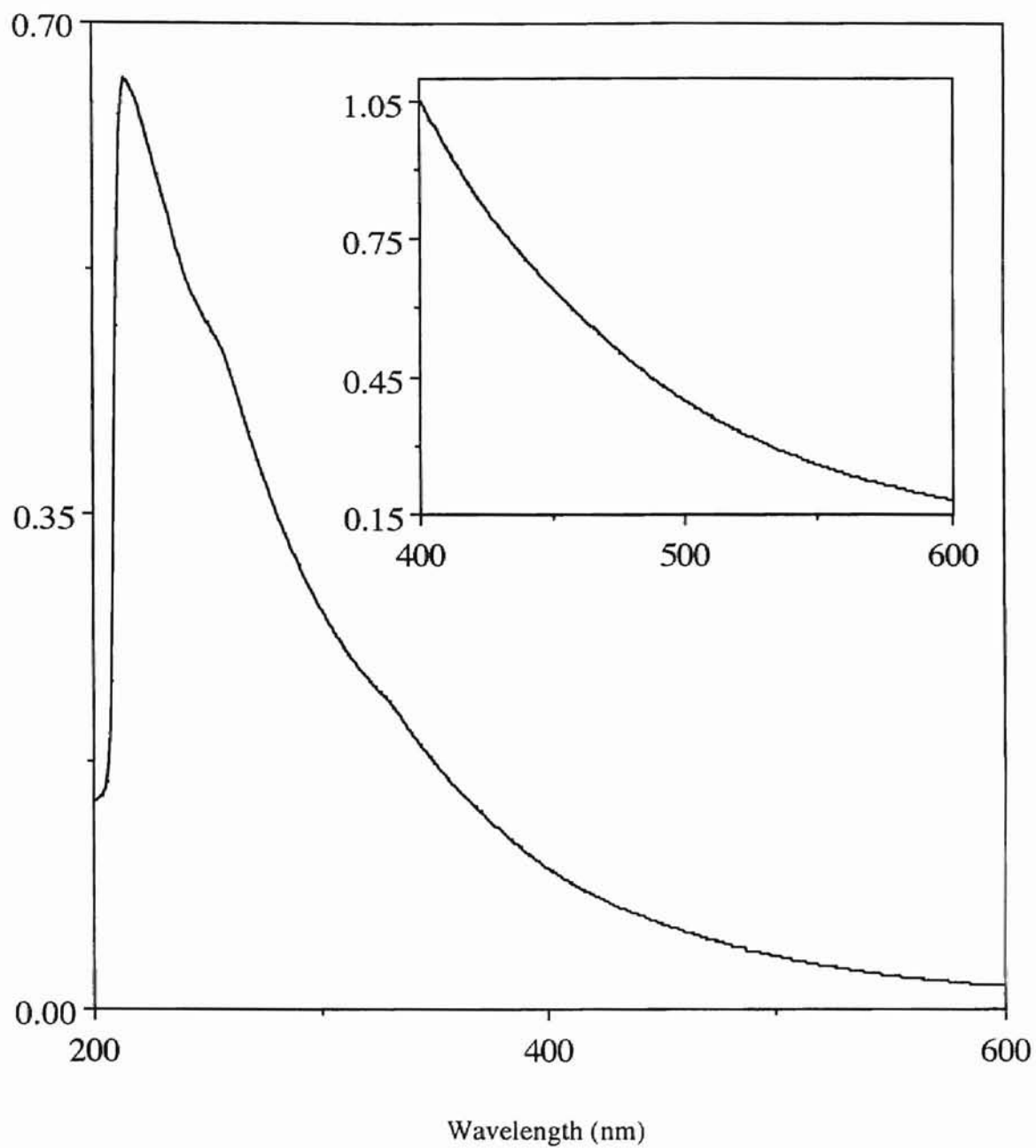


Figure 24. UV-Visible Spectrum of C₆₀(5%)-PS.

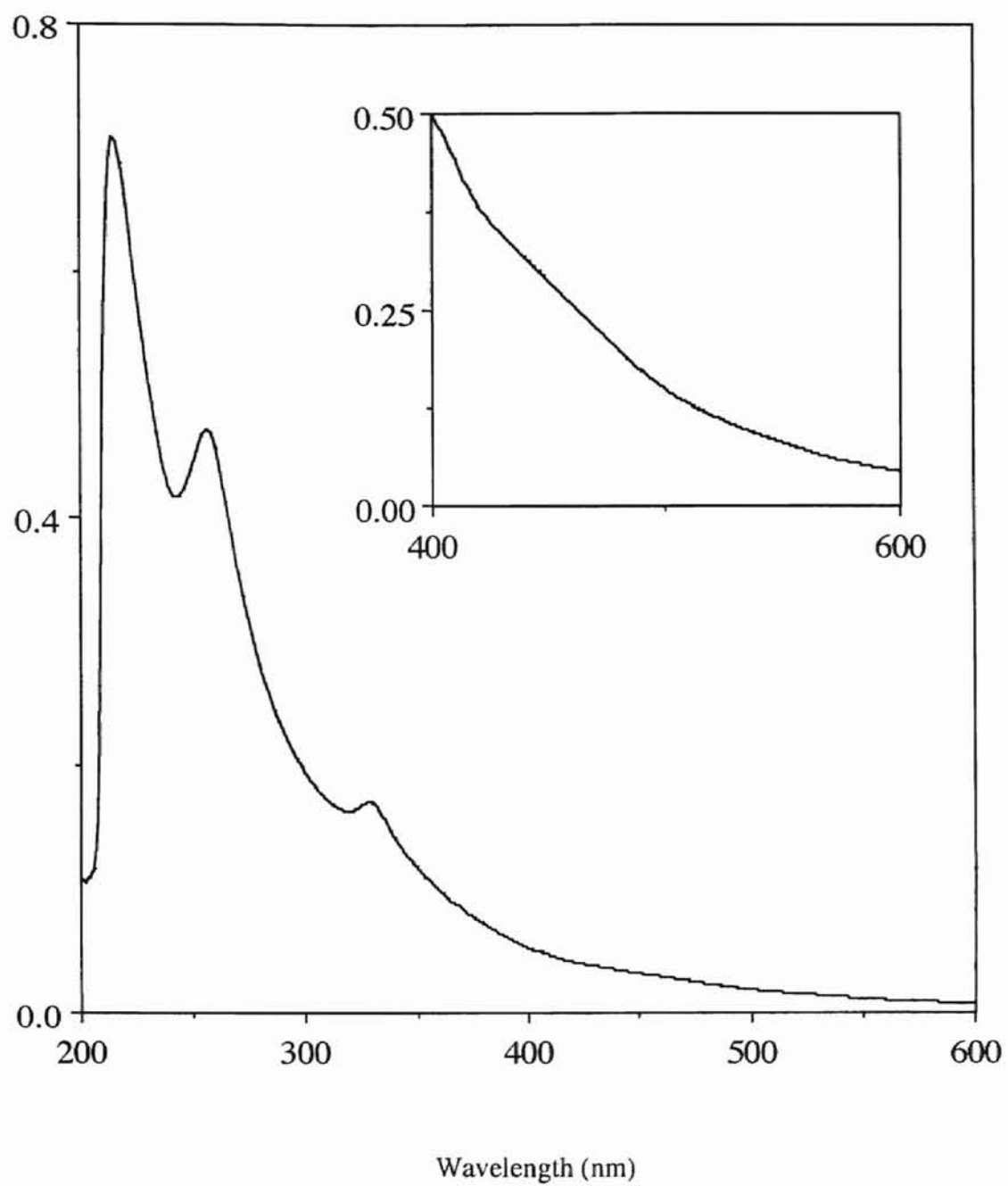


Figure 25. UV-Visible Spectrum of C₆₀(10%)-PS.

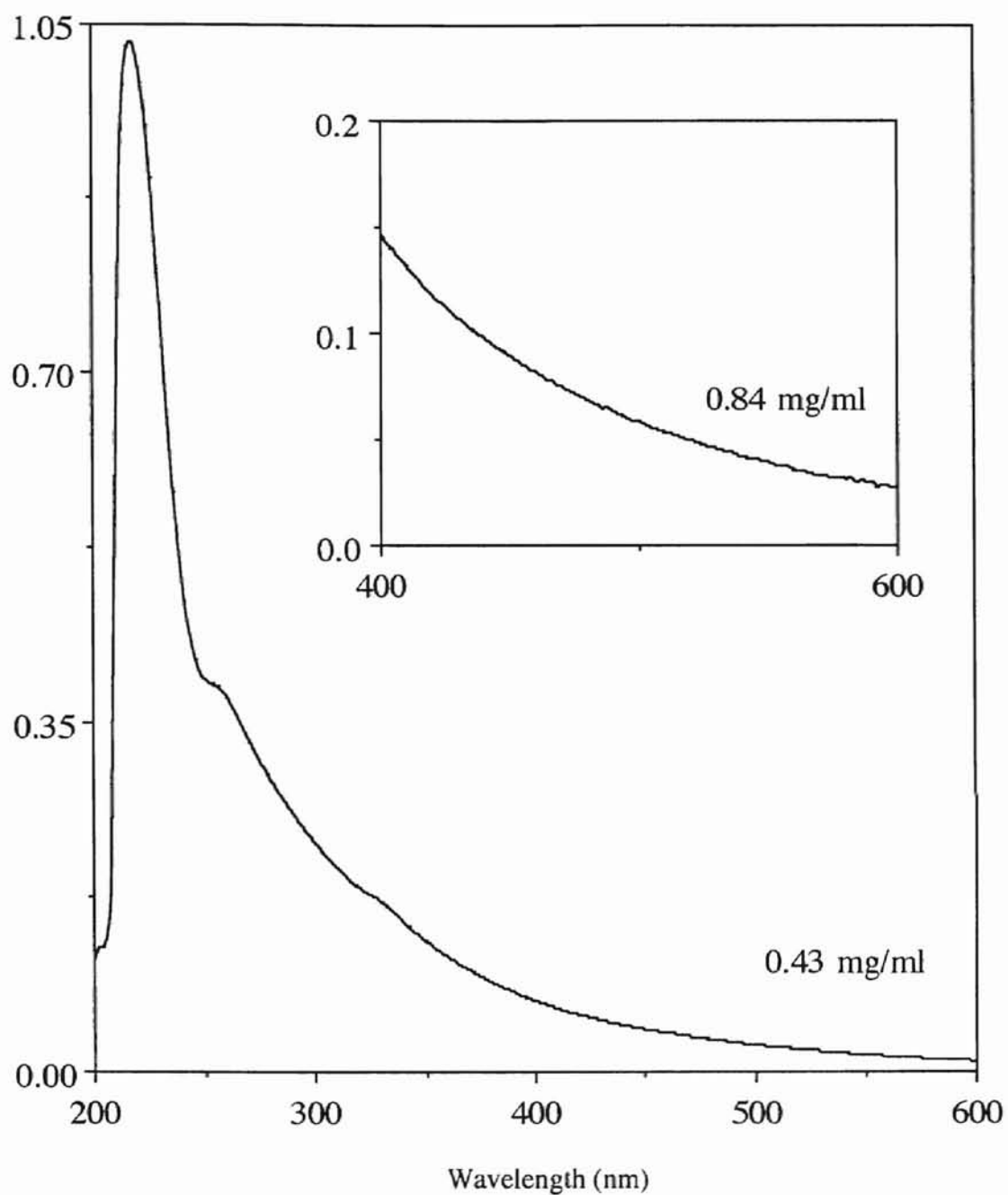


Figure 26. UV-Visible Spectrum of C₆₀(1%)-PMMA.

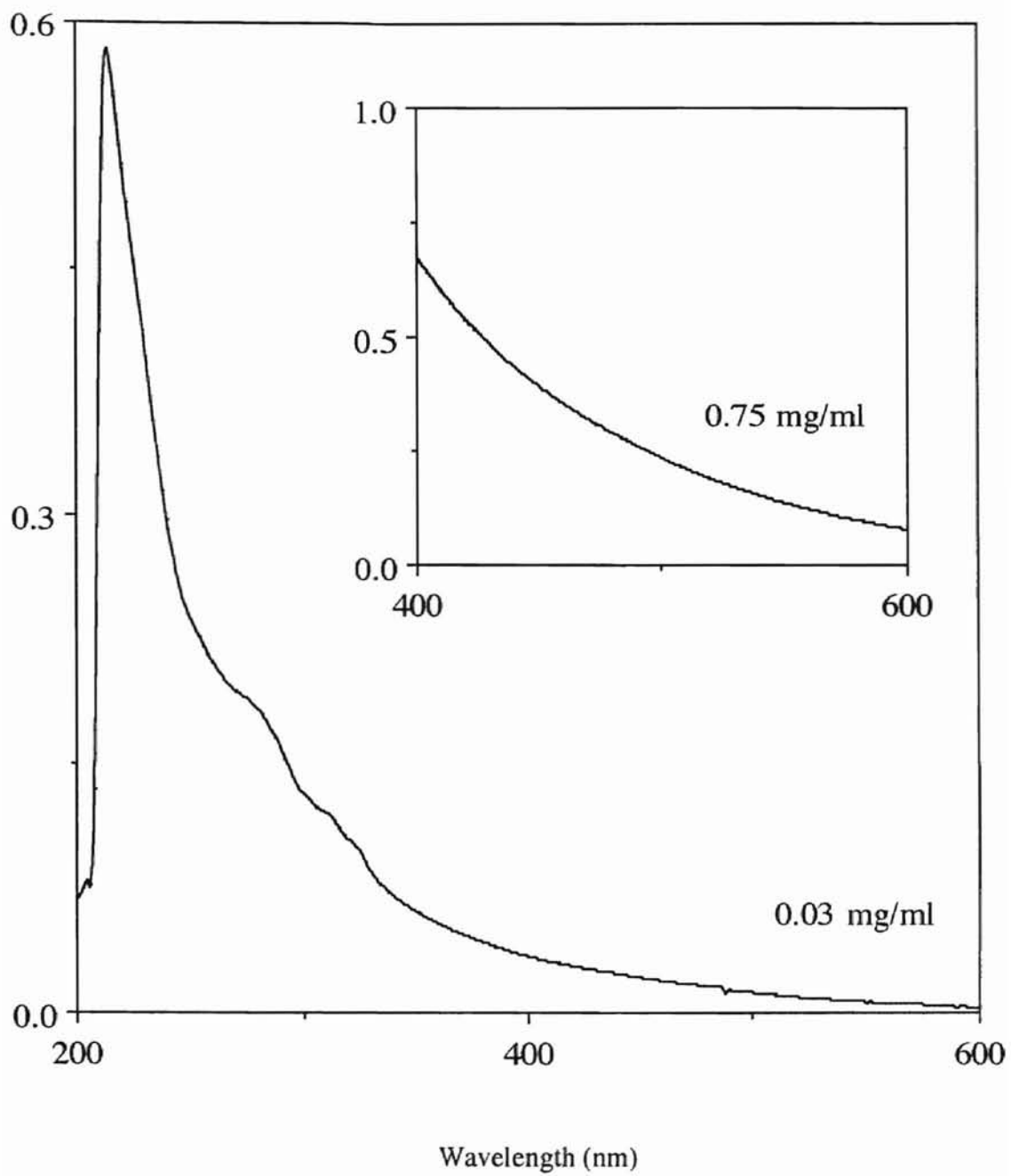


Figure 27. UV-Visible Spectrum of C₆₀(5%)-PMMA.

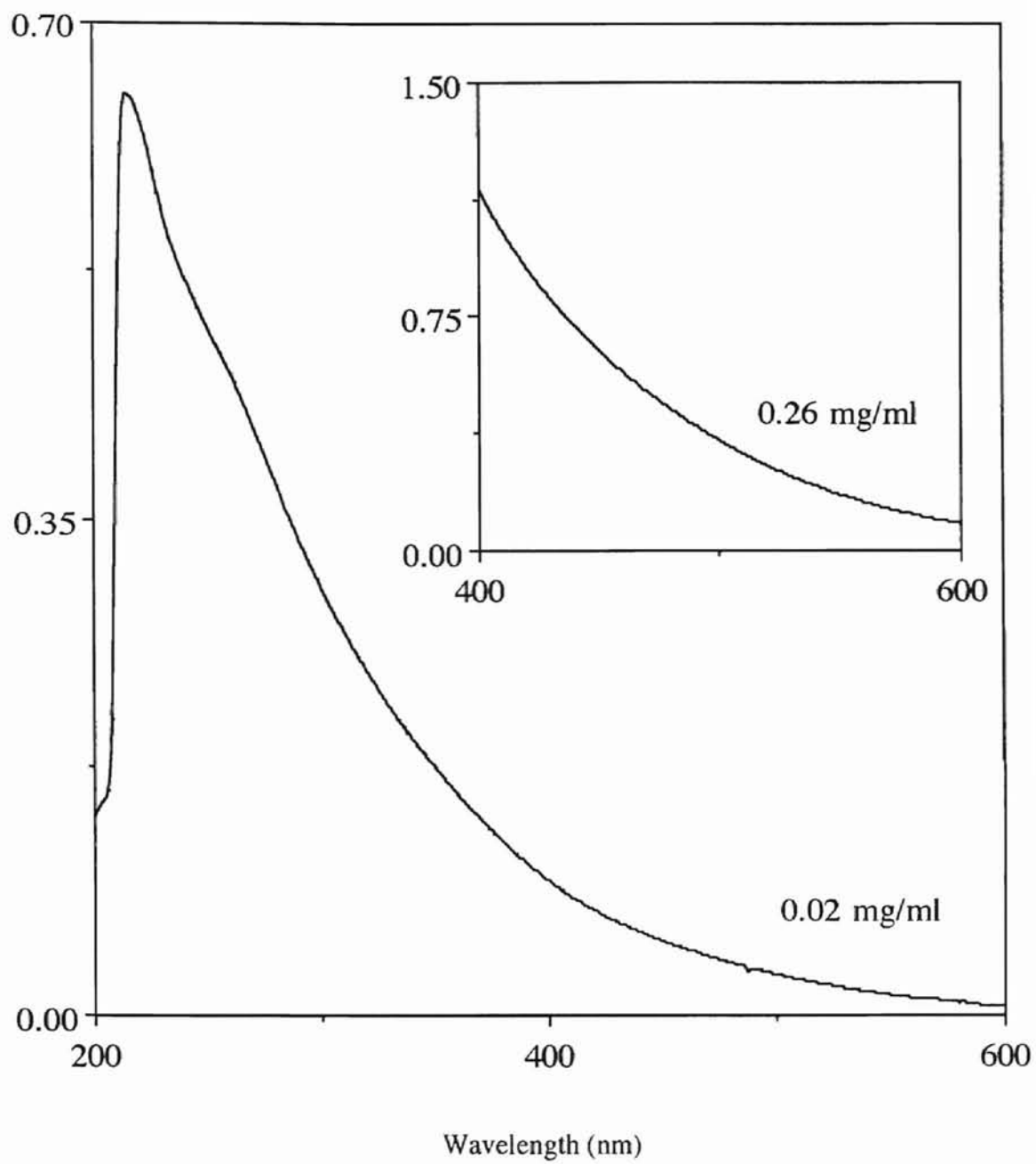


Figure 28. UV-Visible Spectrum of C₆₀(10%)-PMMA.

Table III. Absorptivity values of C₆₀ samples.

Sample	a (ml mg ⁻¹ cm ⁻²) ^a	λ (nm)
1%-PMMA	0.942 ± 0.008	250
	0.171 ± 0.003	400
5%-PMMA	7.390 ± 0.527	250
	1.015 ± 0.118	400
10%-PMMA	22.798 ± 0.505	250
	4.447 ± 0.016	400
C ₆₀ :AIBN (1:5)	45.045 ^b	250
	8.737 ± 0.254	400
1%-PS	11.440 ± 5.240	250
	1.700 ± 0.556	400

^a Median value calculated from several different concentrations. ^b Calculated from only one concentration.

GPC Analyses. Molecular weight determinations have been completed for all C₆₀-containing samples and the PS control samples (Table IV). The chromatograms seem somewhat atypical for a free radical polymerization (Figures 29-32). The first peak is due to polymer with a broad distribution of molecular weights, which is expected for a free radical process. However, the other peaks appear to be individual components of a specific molecular weight.

The chromatograms of the C₆₀ containing PS samples vs. their control samples (Figures 29-31) look similar to each other. The C₆₀-PS products show a decrease in molecular weight with increasing amounts of C₆₀ as seen in Table IV. Furthermore, the incorporation of C₆₀ into PS causes the molecular weights to decrease as compared to the control sample. Notice too, that the molecular weights of the control samples also decrease. In the attempt to maintain a 1:5 molar ratio of C₆₀:AIBN throughout all of the

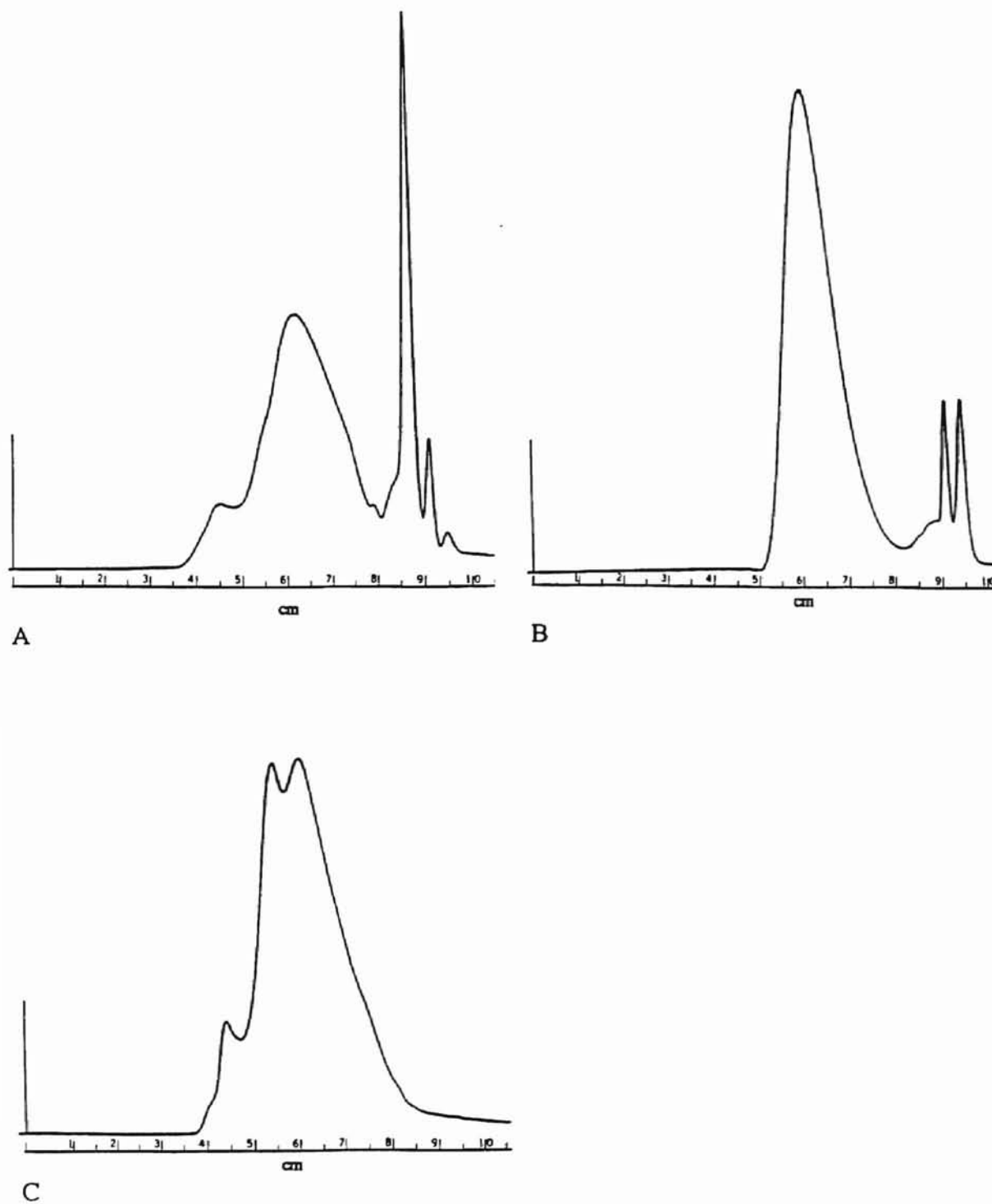


Figure 29. GPC of A) C_{60} (1%)-PS at 249 nm. B) C_{60} (1%)-PS Control at 249 nm.. C) C_{60} (1%)-PS at 400 nm. Chart speed is 0.5 cm/min.

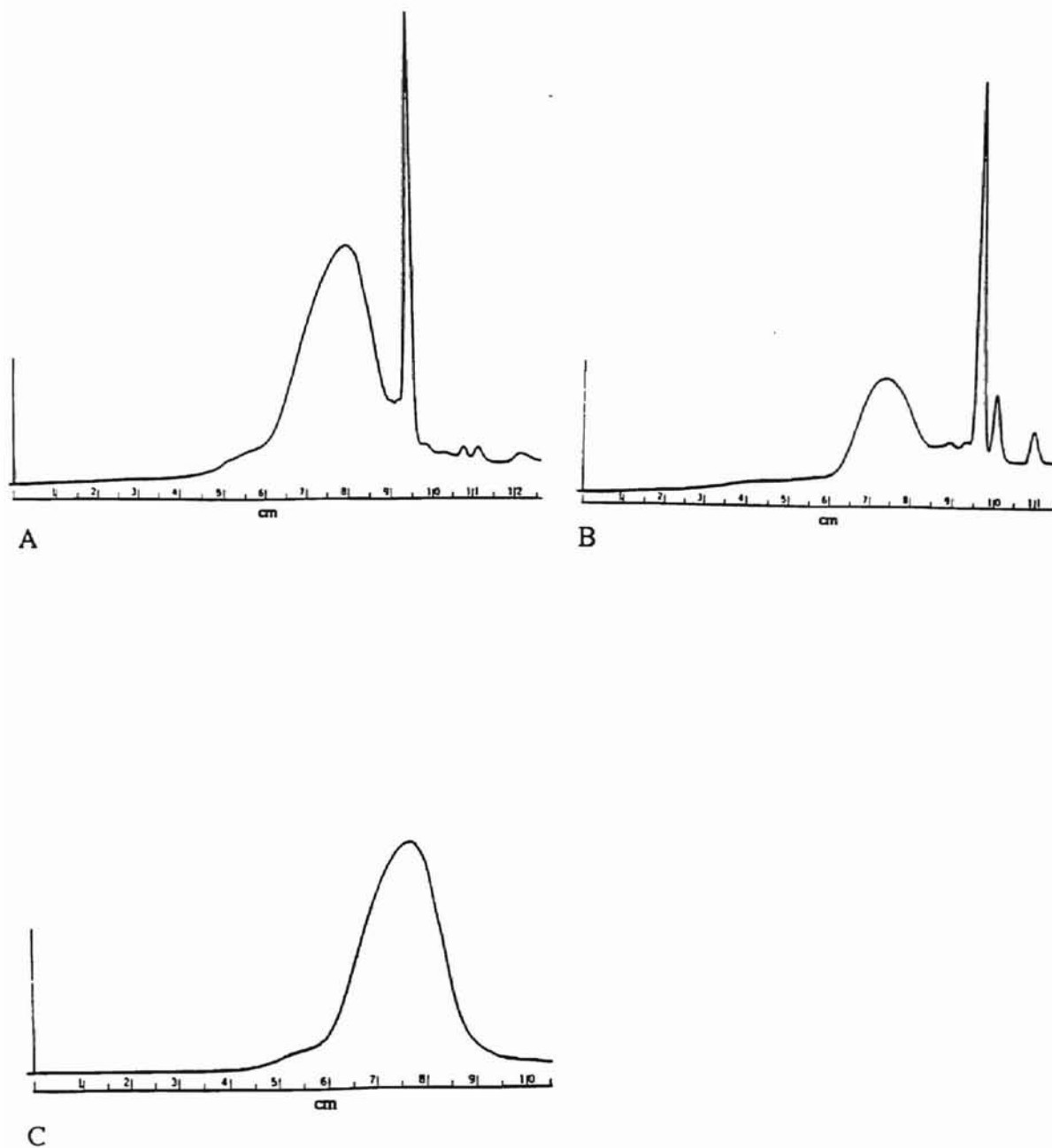


Figure 30. GPC of A) $C_{60}(5\%)-PS$ at 249 nm. B) $C_{60}(5\%)-PS$ Control at 249 nm.. C) $C_{60}(5\%)-PS$ at 400 nm. Chart speed is 0.5 cm/min.

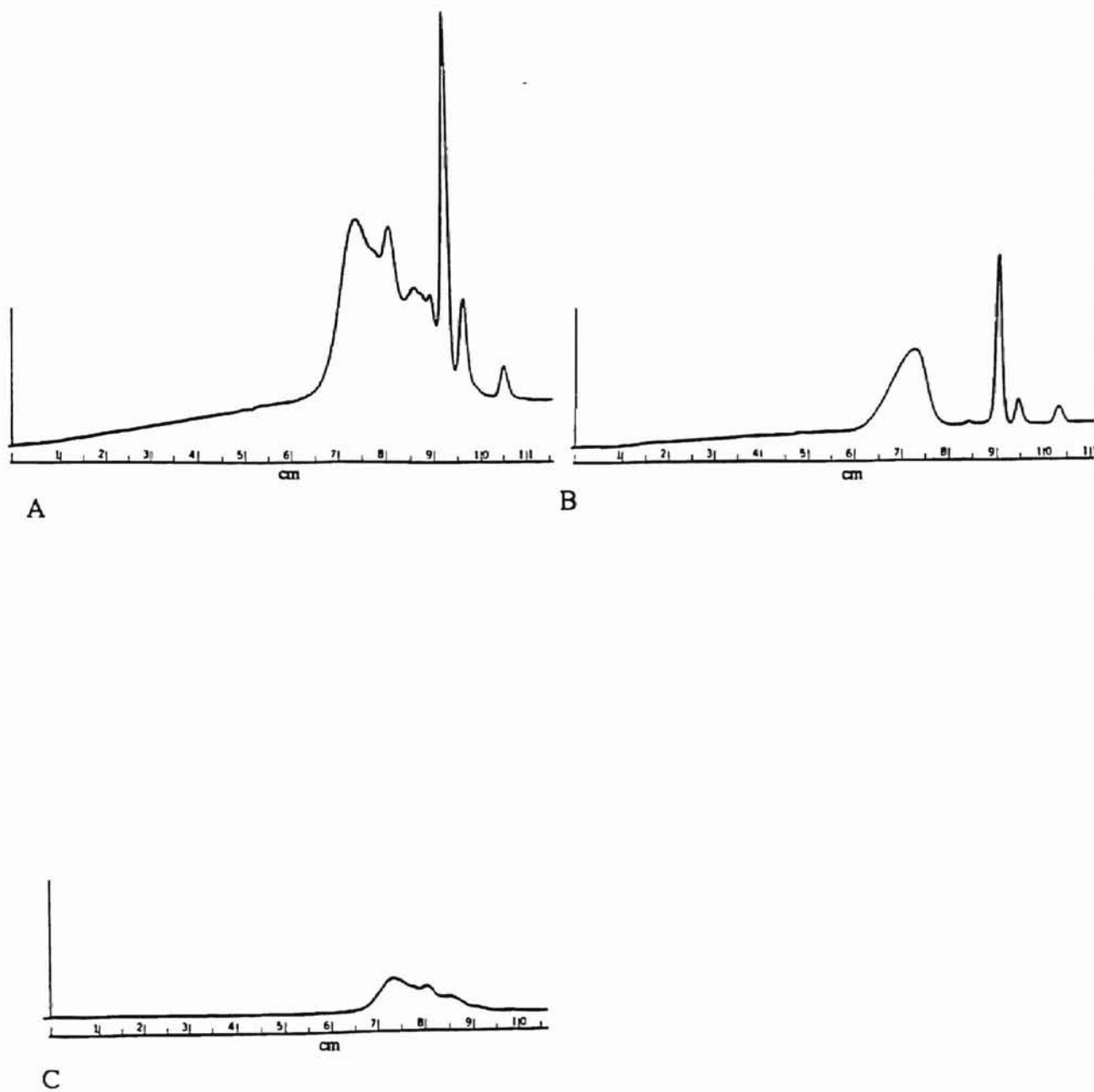


Figure 31. GPC of A) $C_{60}(10\%)-PS$ at 249 nm. B) $C_{60}(10\%)-PS$ Control at 249 nm.. C) $C_{60}(10\%)-PS$ at 400 nm. Chart speed is 0.5 cm/min.

reactions, there is an increasing amount of initiator being used. The effect of using larger amounts of AIBN is a decrease in molecular weight. Additionally, more solvent is needed to dissolve the larger amounts of C₆₀, which creates a dilution problem that further lowers the molecular weight.

At 249 nm, both C₆₀ and PS absorb. In order to determine if the first peak in the chromatograms contain any C₆₀, the polystyrene samples were evaluated at 400 nm, because only C₆₀ will absorb at this wavelength. As expected, the PS control samples showed no absorption at 400 nm. However, the C₆₀ containing samples showed the broad peak at 400 nm just as it did at 249 nm (Figures 29-31c). Therefore, C₆₀ definitely has been covalently incorporated into the polymer. The other peaks appearing in the chromatograms taken at 249 nm must be due to a PS-AIBN component, because they do not appear at the 400 nm wavelength where C₆₀ absorbs.

The PMMA samples containing 1%, 5%, and 10% C₆₀ have chromatograms (Figure 32) that also look similar. These samples show a molecular weight decrease with an increasing amount of C₆₀ as can be seen in Table IV. Another observation from

Table IV. Molecular weights of C₆₀ polymers.

Sample	Mn	Mw	Mw/Mn
C ₆₀ (1%)-PMMA	18200	34600	1.9
C ₆₀ (5%)-PMMA	4200	7960	1.9
C ₆₀ (10%)-PMMA	2250	3160	1.4
C ₆₀ (1%)-PS control	16400	26700	1.6
C ₆₀ (1%)-PS	9780	24700	2.5
C ₆₀ (5%)-PS control	3960	5720	1.4
C ₆₀ (5%)-PS	900	1670	1.8
C ₆₀ (10%)-PS control	2980	3630	1.2
C ₆₀ (10%)-PS	1810	2530	1.4

Table IV is that the PMMA samples have a higher molecular weight than the corresponding PS samples.

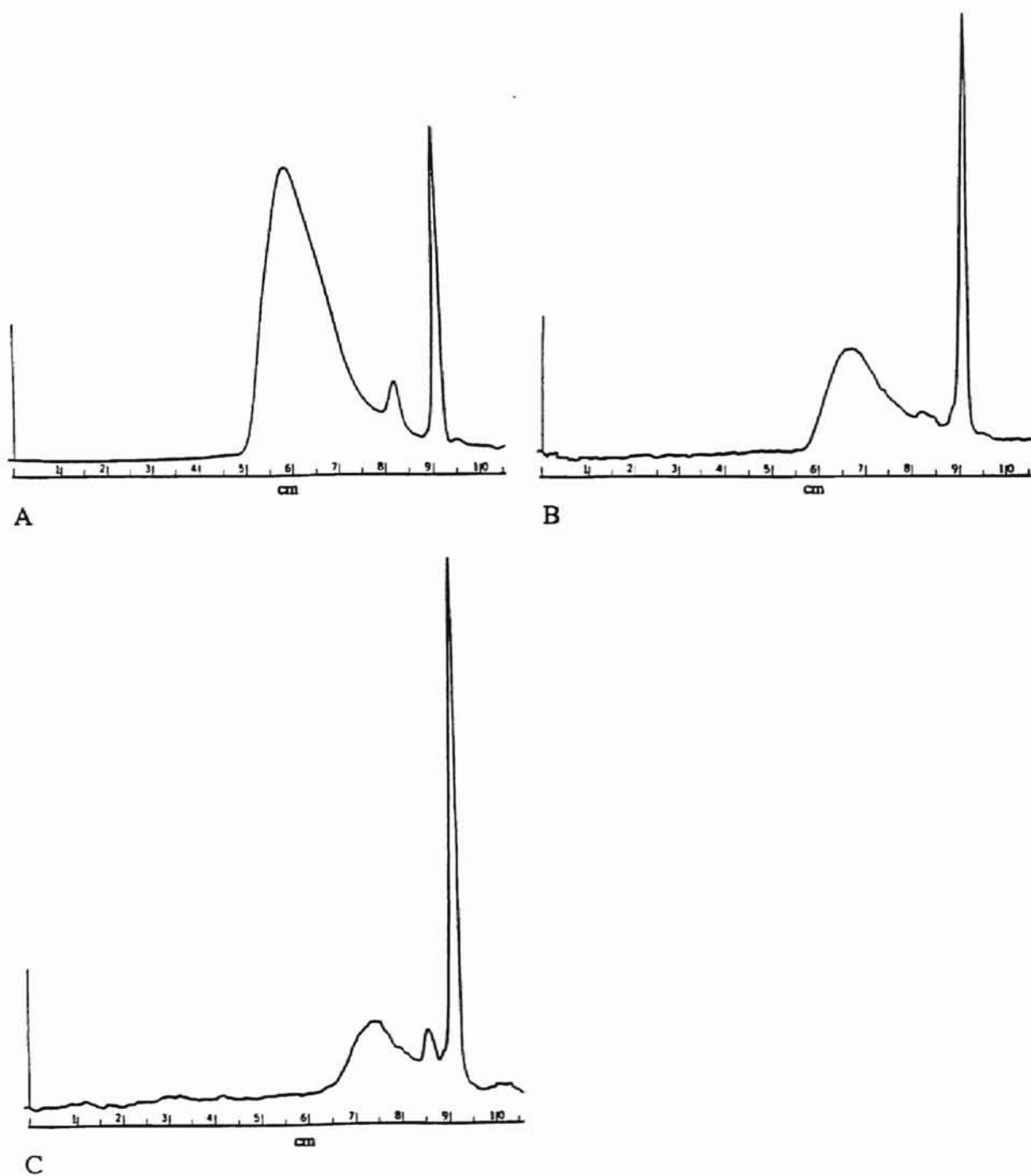


Figure 32. GPC of A) C₆₀(1%)-PMMA. B) C₆₀(5%)-PMMA. C) C₆₀(10%)-PMMA. Chart speed is 0.5 cm/min.

NMR Analyses. The ^1H and ^{13}C spectra of C_{60} (1%)-polymer samples are indistinguishable from the control samples. Due to the poor solubility of the 5 and 10 % C_{60} -PS samples, adequate spectra were not obtained. The spectrum for the 5% C_{60} -PMMA sample showed no C_{60} peak, and it was identical to the corresponding control sample. Figure 33 contains the ^{13}C spectrum for 10% C_{60} -PMMA. The spectrum was obtained using an acquisition time of 1 sec, pulse width of 25.0 μsec , delay of 2.0 sec, and 23232 transients. The PMMA peaks appearing in the spectrum are 16-18 ppm ($-\text{CH}_3$), 44 ppm (CH_2), 53 ppm ($-\text{OCH}_3$), 55 ppm ($\text{C}=\text{CH}_2$), and 178-180 ppm ($\text{C}=\text{O}$). However, the spectrum showed some peaks that were not found in the spectrum for the control. The shaded areas identify the peaks which are different from PMMA. Around 22-30, 38-40, 70-72 ppm and 122-158 ppm, broad bands in the baseline of the spectrum appear. These new peaks are due to derivatized C_{60} . The small sharper peaks around 125-128 ppm are due to the solvent o-dichlorobenzene. This conclusion is based on the ^{13}C spectrum of C_{60} :AIBN (1:5) shown in Figure 34. The spectrum shows the same broad bands at 22-30, 38-40, 70-72 ppm and 122-158 ppm. Sharp peaks also appear at 23, 39, 121, 127, 130, and 132 ppm. The broad band upfield at 22-32 ppm is assigned to the $-\text{CH}_3$ of AIBN radicals bonded to C_{60} . The 37-42 ppm resonance is attributed to the quaternary carbon of AIBN, and the 121-127 region is due to $-\text{CN}$. C_{60} aliphatic carbons are assigned to 70-73 ppm, and the double bond carbons of C_{60} appear at 130-160 ppm. The product of two AIBN radicals recombining is called tetramethylsuccinonitrile. The ^{13}C chemical shifts of this compound have been reported.⁴⁷ Based on this report, the assignments for the sharp peaks were made. The peak at 23 ppm is the $-\text{CH}_3$ of tetramethylsuccinonitrile, 39 ppm is the quaternary carbon, 121 ppm is the $-\text{CN}$, and the other three peaks are ODCB. The ^1H spectrum for this sample is located in Figure 35. A broad band appears from 1.4 to 2.2 ppm which is attributed to the methyl protons of AIBN radicals bonded to C_{60} . If the AIBN fragments attached to C_{60} have hindered rotation and multiple additions have occurred, then a broad band would be reasonable.

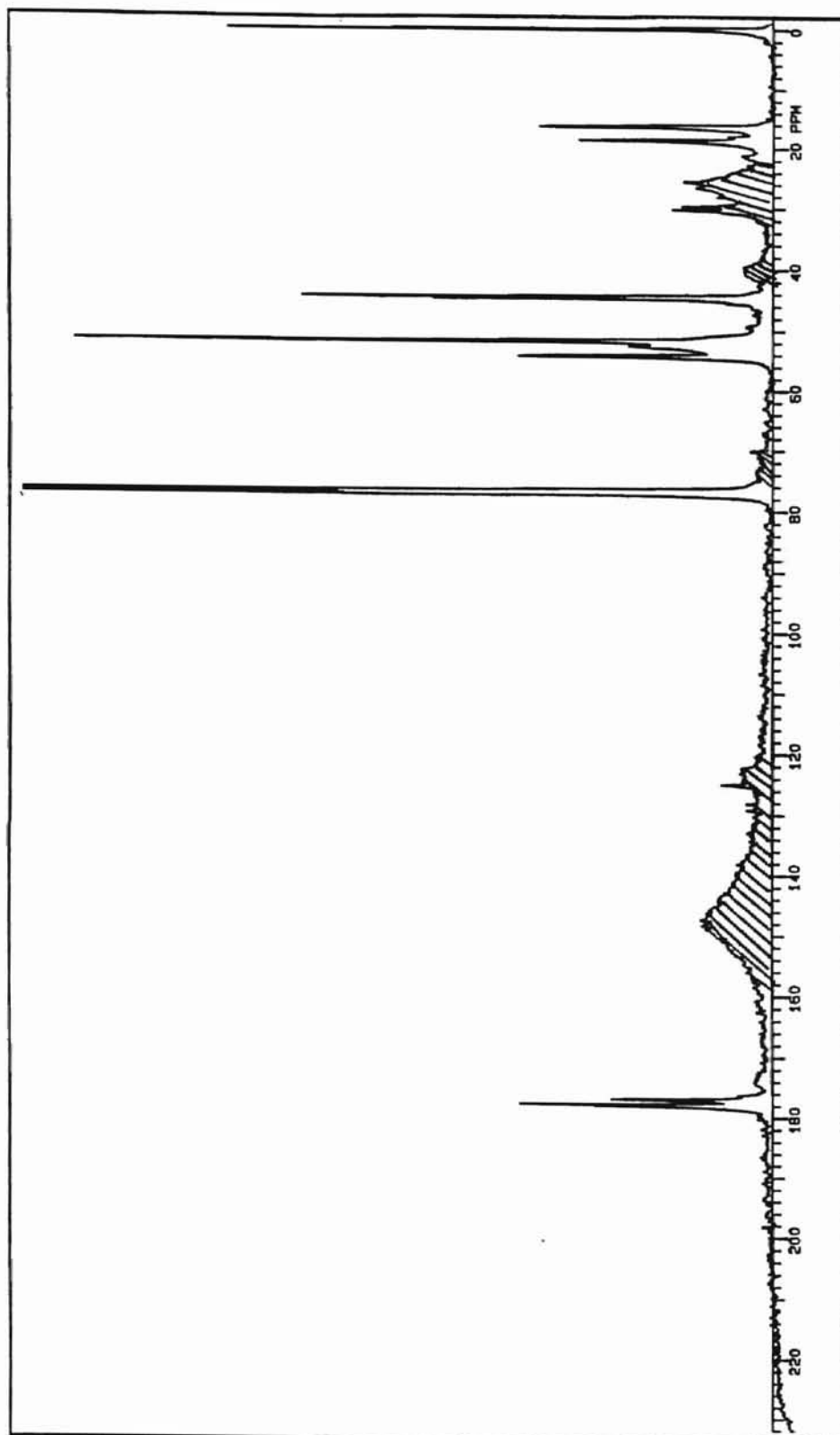


Figure 33. ^{13}C spectrum of 10% C_{60} -PMMA in CDCl_3 .

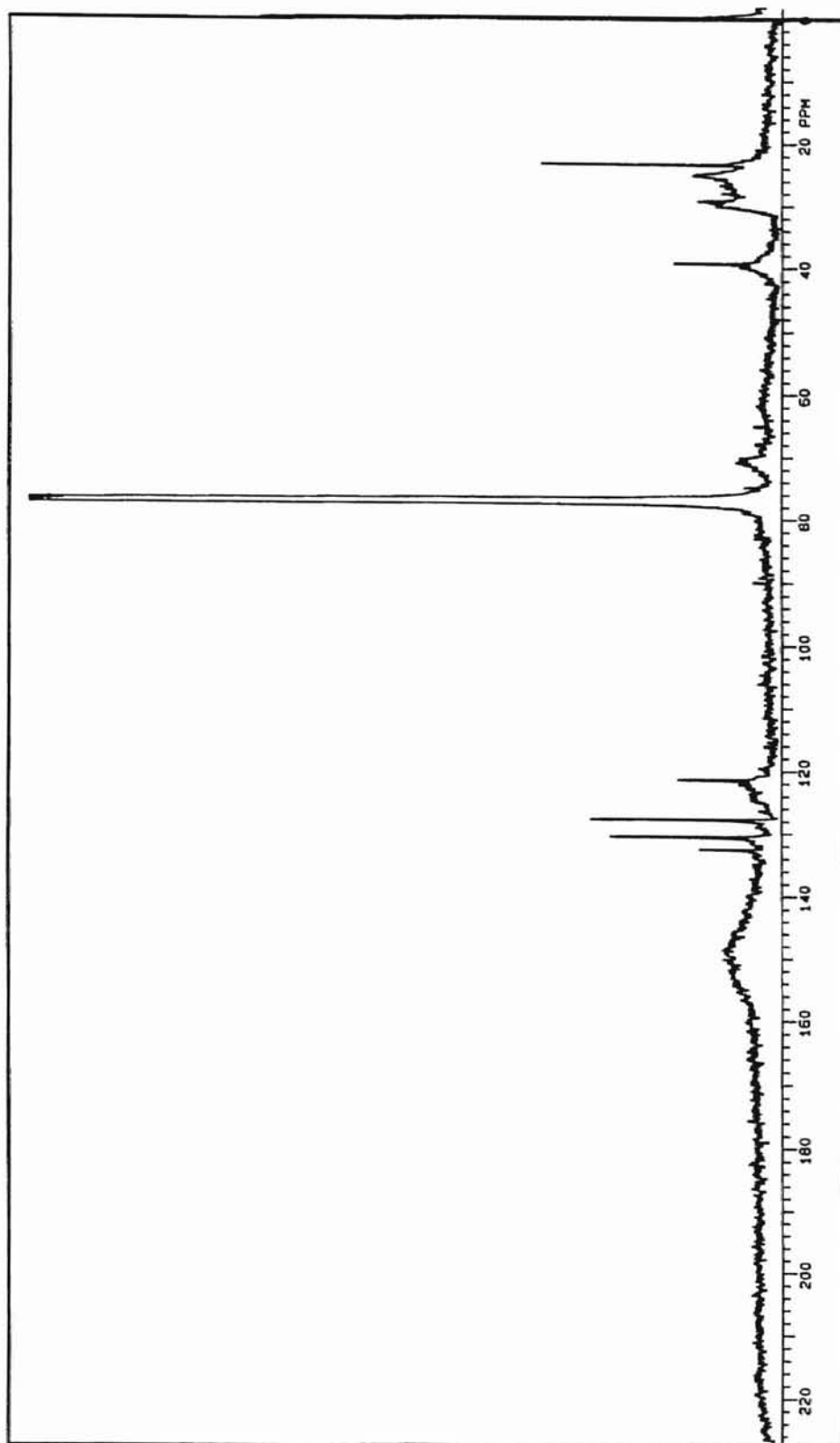


Figure 34. ^{13}C spectrum of C_{60} :AIBN (1:5) in CDCl_3 .

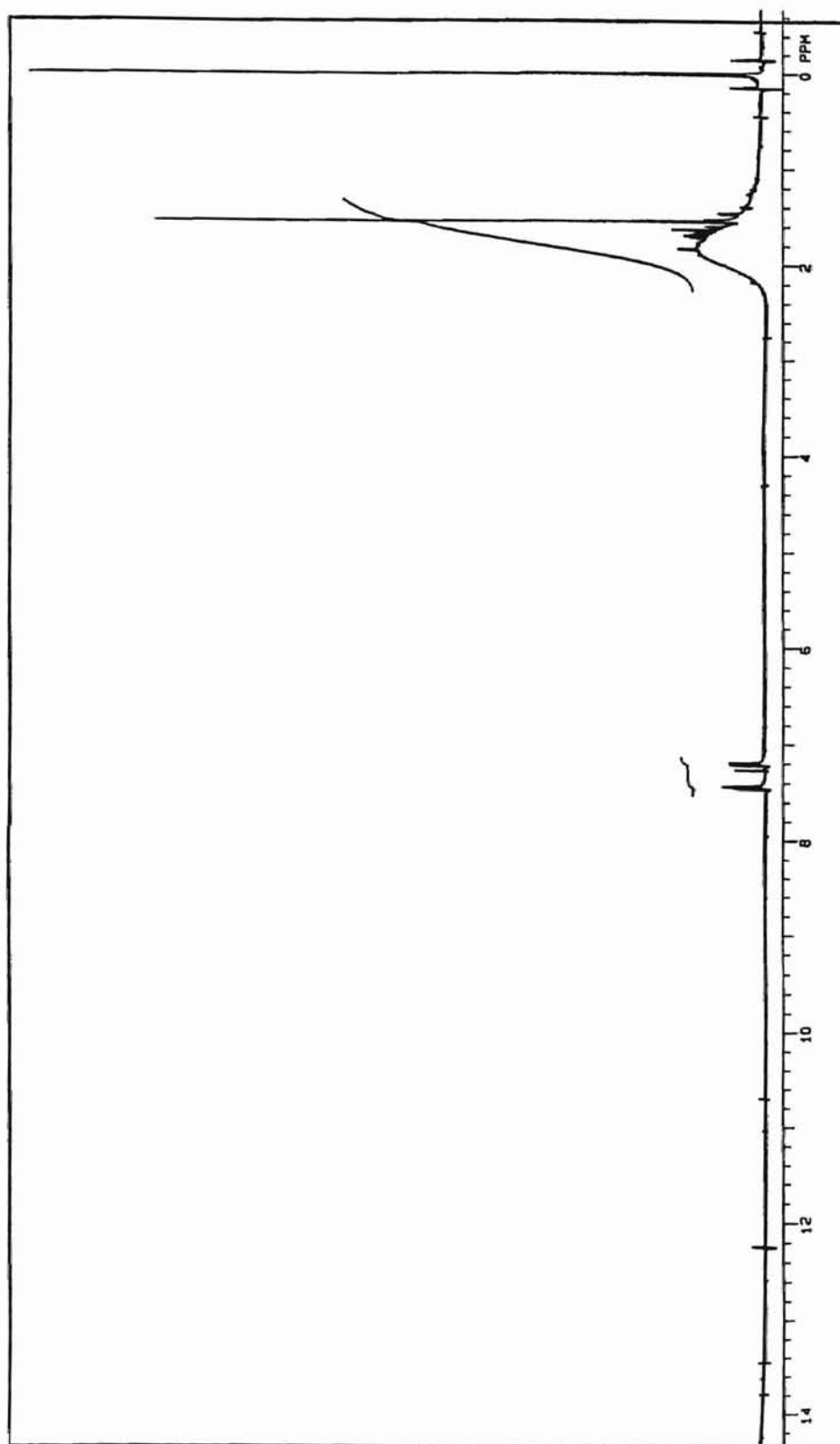


Figure 35. ^1H spectrum of C_{60} :AIBN (1:5) in CDCl_3 .

There is a tall sharp peak at 1.6 ppm, which is due to tetramethylsuccinonitrile. The spectrum also shows resonance in the aromatic region which is due to ODCB.

The NMR data for all polymer samples do not provide much information. With only 1wt% C₆₀ incorporated, the spectra of the polymers look like the spectra of the polymers containing no C₆₀. At 10 wt% C₆₀ incorporation, some differences are seen; however, these differences are also seen in the C₆₀:AIBN compound.

DISCUSSION

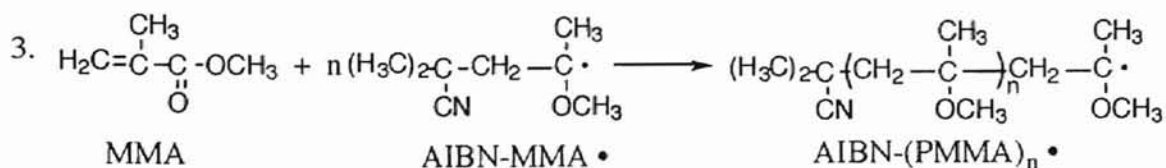
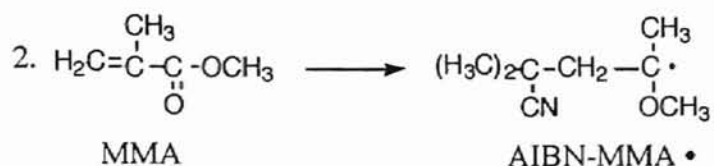
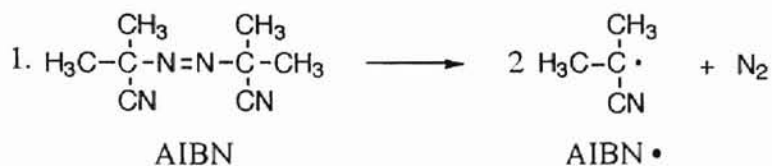
The PMMA reactions produced products which are readily soluble in common organic solvents. However, the styrene reactions only gave completely soluble products at the 1 wt% C₆₀ level of incorporation. The yields for the 1 and 5% PMMA samples were respectable at ~ 65% but fell miserably to less than 10 % at the 10% C₆₀ level. The yields for the PS samples were all below 10%.

The FTIR analyses were not able to identify any C₆₀ incorporation into the polymer samples. However, the samples obtained from the C₆₀:AIBN reactions clearly showed that more derivatization occurs at a 1:5 molar ratio than a 5:1 ratio. The 5:1 sample not only shows distinct C₆₀ peaks but it also has solubility behavior similar to that of C₆₀ itself. Whereas, the 1:5 sample shows no C₆₀ peaks, and it has good solubility.

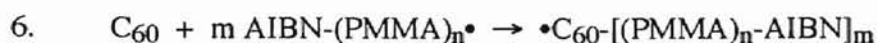
The UV-Visible analyses provided the first evidence of C₆₀ derivitization. From the spectra, it can be seen that the C₆₀ electronic structure has been changed. The individual peaks for C₆₀ are lost and replaced by a maximum absorption between 200-230 nm followed by tailing absorption. However, the 5:1 C₆₀:AIBN and the 10% PS sample show definite C₆₀ peaks.

The GPC results indicates that C₆₀ has been incorporated into the polymer because the broad distribution pattern found at 250 nm is retained at 400 nm -- wavelength where PS doesn't absorb. The molecular weight calculations show that C₆₀ causes a decrease in molecular weights. The C₆₀-containing PS samples all have molecular weights lower than the control samples, and as the amount of C₆₀ increases the molecular weights decrease for both the PS and PMMA products. The 5 and 10% C₆₀-PS samples have such low molecular weights that they can not truly be considered polymeric. This conclusion for the 10% sample is also justified by its UV-vis spectrum. The C₆₀-PMMA samples seem to be more promising than the C₆₀-PS samples. They have higher molecular weights, and the materials are completely soluble even at 5 and 10% C₆₀ incorporation. Both of these factors are desirable for C₆₀ polymeric derivatives.

None of the analyses done so far gives any conclusive information on the structure of these products. However, based on the results and what is known from the literature, some possible structures can be proposed. Using methyl methacrylate as an example, possible routes to product formation might be as follows:



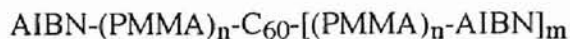
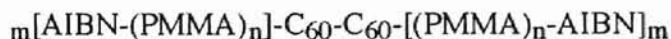
AIBN loses nitrogen to form the AIBN radical in equation 1. The radical then reacts with MMA to eventually form a radical PMMA chain as in equation 3. Any one or all of these radicals could react with C₆₀ to create C₆₀ radical adducts as shown in equations 4-6.



It is possible that any of these radical adducts could react with more monomer to propagate the polymer chain (Equation 7).



Obviously, there could be many possible termination steps. Some examples of termination are as follows:



Termination by disproportionation is also a possibility.



There are also non-C₆₀ containing products that could form. For example, the AIBN radical could terminate a growing polymer chains as in equation 12. Two polymer chains could terminate (Equation 13), or two AIBN fragments could recombine as in equation 14.



It is possible that these products could be arranged as star-shaped, branched, or linear polymers. No doubt the samples are actually mixtures of products. Therefore, characterization would require a separation process such as preparative HPLC followed by one and two dimensional NMR analyses of the fractionated polymers.

Monofunctionalized C₆₀ polymers, which were discussed in the introduction, are easier to characterize than polymers formed by multiple additions to C₆₀ such as in a free radical process. For example, monofunctionalized C₆₀ polymers have a UV-Vis spectrum with distinct peaks and NMR spectra with C₆₀ peaks in the 133 to 145 ppm region. Characterization of products from free radical reactions have not been as conclusive. However, the results obtained from this research are consistent with the results reported by Cao and Webber³³ and Sun³⁴ after the experimental work in this thesis was finished. Both of these groups studied the free radical initiation of C₆₀ with styrene. The experimental conditions from the Cao and Webber study were similar to the conditions reported herein. Polymerizations were done at 60-65 °C for 12-24 hours using deoxygenated solutions. Products were precipitated in heptane (2x) and then into methanol (1x). The conditions reported by Sun were 65 °C for 32 hours followed by precipitation into methanol. There was no mention of deoxygenating solutions. The discoveries of their research are summarized in the text below.

Cao and Webber

1. Solution polymerization of ~ 1 wt% C₆₀ and styrene produces a soluble copolymer in 16% yield with a Mw of 14,400.
2. The SEC traces do not show separate components (oligomers).
3. The UV-visible spectrum showed a structureless absorption pattern with a strong absorption between 200-230 nm.

Sun

1. They found no oligomers at low percentages of C₆₀, but at 17 wt% the polymer does contain oligomers.
2. The yields for the low percentages of C₆₀ were fairly good (~ 55%) and poor (~ 10%) for the highest wt% of C₆₀.
3. The FTIR and NMR spectra of the copolymers are nearly the same as those of neat polystyrene.
4. There was a loss of C₆₀ absorption peaks in the UV-vis to the structureless pattern with a decreasing curve of absorption. With increasing amounts of C₆₀, the spectra show broader absorption.

CONCLUSIONS

C_{60} copolymerizes with methyl methacrylate and styrene monomers. However, with polystyrene, polymerization seems only to occur at a low wt% of C_{60} ; only at the 1% level are the products completely soluble. The methyl methacrylate reactions are easier to work with because they produce soluble products even at 10 wt% C_{60} incorporation. Unlike the styrene reactions, good yields are obtained with MMA using 1 and 5% C_{60} but not with 10%. Another advantage is that the molecular weights of the C_{60} -PMMA products are higher than the C_{60} -PS ones. The weight average molecular weights are 18,200, 4,200, and 2,250 for 1, 5, and 10 wt% C_{60} -PMMA samples respectively. In the future, it would be more promising to focus on reactions using the methyl methacrylate because of the higher yields, higher molecular weights, and soluble products obtained.

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