Structure and Radical Mechanism of Formation of Copolymers of C_{60} with Styrene and with Methyl Methacrylate

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ABSTRACT: Polymerizations in 1,2-dichlorobenzene solutions containing 0.33 volume fraction of styrene or methyl methacrylate (MMA) and relative weights of monomer/C_{60}/azo(bisisobutyronitrile) (AIBN) of 100:1.00:1.12 at 75 °C form high molecular weight materials in which all of the C_{60} is incorporated covalently. To understand the structures of the polymers and their mechanism of formation, samples were isolated after low conversion of monomer and analyzed. Molar size exclusion chromatograms from UV detection of fullerenes, differential refractive index detection of the mass of the polymer, and differential viscometry detection of the specific solution viscosity of the polymer show that the fullerene reacts rapidly, and both polystyrene/C_{60} and PMMA/C_{60} products isolated after low conversion of monomer contain many fullerenes per molecule. Lower intrinsic viscosity and higher absolute molecular weight of the fullerene-containing polymers compared with linear polystyrenes at equal retention time show that the polymer structures are branched. Elemental analyses, NMR spectra, and size exclusion chromatograms show that the C_{60} content is higher and the polymer chain lengths are shorter in the low-conversion polystyrene/C_{60} than in the low-conversion PMMA/C_{60}. C_{60} itself polymerizes when initiated by AIBN. NMR analyses of polymers formed by initiation with AIBN-α-^{13}C show that in both polystyrene/C_{60} and PMMA/C_{60} at low conversion 62−72% of the 2-cyano-2-propyl groups are bound to polymer chain ends, and 28−38% are bound to fullerenes. Neither low molar mass AIBN/C_{60} adducts nor the polymers at any degree of conversion initiate further polymerization of monomer. Thus, the formation of 2-cyano-2-propyl to fullerene and polymer to fullerene carbon−carbon bonds is irreversible. After high conversion both polystyrene/C_{60} and PMMA/C_{60} contain much linear polymer. The average number of fullerene units per molecule decreases with increasing reaction time, and after complete reaction of monomer, all polystyrene/C_{60} samples and some PMMA/C_{60} samples still have an average of more than one fullerene unit per macromolecule at the high end of the molecular weight distribution. Fullerene radicals were detected by ESR spectroscopy in all of the solid polymers recovered at low and high conversion. Evaluation of a radical chain mechanism for the copolymerizations using estimated rate constants for the microscopic steps shows that the fullerene must exist as clusters early in the polymerization, and that the clusters break down to macromolecules containing smaller numbers of fullerene units as the polymerization continues.

Introduction

Polymers containing fullerenes, particularly the most abundant C_{60}, offer opportunities for the production of new optical and electroactive materials that can be processed into shaped objects and thin films.[1−6] The linear and nonlinear absorption and emission of fullerenes from the UV to the near infrared via excited singlet and triplet states can be varied widely by derivatization.[7] Fullerenes serve as electron acceptors from electron-rich polymers in composites that show promise for solar energy conversion.[8] One problem in the preparation of composite materials is that the parent C_{60} has low or no solubility in most solvents and tends to aggregate when it does dissolve.[9,10] The solubility problems often can be avoided by functionalization of C_{60} with low molar mass substituents or polymer chains.

C_{60} has been incorporated covalently into polymers by a variety of reactions as part of the main chain, at the ends of side chains, as end groups, as branch points of stars, and as junctions of networks.[1−6] Homopolymers of C_{60} can be formed by UV−vis irradiation or high-pressure compression and converted thermally back to monomeric C_{60}.[11,12] The easiest method of incorporation of C_{60} into a polymer is radical copolymerization, which can produce materials of widely varied fullerene content, but the degree of substitution of the fullerene is hard to control, and the structures are heterogeneous and hard to determine.[13−21]

Multidetector size exclusion chromatographic (SEC) analyses of polystyrene/C_{60} and PMMA/C_{60} produced thermally by azobis(isobutyronitrile) (AIBN) initiated polymerization show that the polymers have branched structures.[20] The C_{60} is fully incorporated and the structures are branched after as little as 10% conversion of monomers. After high conversion the products contain a large amount of linear polymer, have weight average molecular weights of 30000−70000, and can be used to form clear brown polymer films. In this paper we report elemental compositions, SEC analyses, and NMR spectra of ^{13}C-labeled polymers formed by polymerization of mixtures containing molar ratios of C_{60}/AIBN/

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Table 1. Materials in Low-Conversion Polymerizations

experiment	mg of C_{60}	monomer (g)	mg of AIBN	mL of oDCB	time at 75 °C (min)	yield[a] (%)
PS30	400	styrene (40)	448	80	30	0.9[b]
PS120	100	styrene (10)	112	20	120	1.9[d]
PS120-^{13}C[c]	25	styrene (2.5)	28	5	120	2.2
PMMA30	400	MMA (40)	448	80	30	0.9
PMMA30-^{13}C[c]	25	MMA (2.5)	28	5	30	1.2
PMMA120	100	MMA (10)	112	20	120	6.1
PMMA120-^{13}C[c]	25	MMA (2.5)	28	5	120	3.9

[a] Products were insoluble in hexane and soluble in THF unless noted otherwise. Yields are based on combined weights of monomer and C_{60}. [b] Fraction insoluble in both hexane and THF; 0.1% of hexane-insoluble/THF-soluble product was isolated too. [c] From AIBN 97% ^{13}C-enriched at the central C atom. [d] 0.3% of product insoluble in both hexane and THF was isolated too.

monomer of 1:5:700 (1 wt % C_{60} relative to monomer) in 1,2-dichlorobenzene (oDCB) solutions to conversions of less than 10% of the monomer and conversion of most or all of the C_{60}, and interpret the compositions and structures in terms of a detailed radical mechanism of polymerization.

Experimental Section

Instruments. ^1H NMR spectra at 300 and 400 MHz and ^{13}C NMR spectra at 75 and 100 MHz were obtained with $CDCl_3$ solutions. Quantitative ^{13}C spectra were obtained with ^1H decoupling only during acquisition, with and without $Cr(acac)_3$ to speed relaxation, and with relaxation delays of 2−5 s. All of these procedures gave the same results. Elemental analyses were performed at Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. Because of possible incomplete combustion of fullerene materials, the samples were heated in oxygen at 1200 °C with a catalyst.

Materials. Monomers were distilled at reduced pressure before use. Reagent grade solvents were used without further purification. C_{60} (99.5%) was from MER Corp., Tucson, AZ. AIBN (Aldrich Chemical Co.) was recrystallized from ethanol at ≤50 °C. 9,10-Dimethylanthracene (DMA) was used as received from Aldrich. Acetone-2-^{13}C (97% enriched) was from Cambridge Isotope Laboratory, Inc. The ^{13}C-enriched AIBN was synthesized in 37% yield (260 mg) from 500 mg of 97% ^{13}C═O enriched acetone, sodium cyanide, and hydrazine sulfate to give 1,2-di-2-(2-cyanopropyl)hydrazine followed by bromine oxidation[22,23] and purified by recrystallization from ethanol. ^1H NMR: 1.73 ppm, d, $J = 4.5$ Hz. $^{13}C[^1H]$ NMR: 68.2 ppm, s.

Copolymerizations. Standard Conditions. All experiments were conducted with relative molar amounts C_{60}:AIBN:monomer = 1:5:700. The weights of materials used are listed in Table 1. C_{60} was dissolved in oDCB, and the solution was stirred under nitrogen for 30 min. AIBN was dissolved in oDCB, the solutions were combined, and monomer was added. The mixture was purged with nitrogen for 5 min and then placed in an oil bath at 75 °C. After the specified reaction time the mixture was cooled to room temperature immediately. A 1.0 mL portion of the solution was removed, and 10 mg of hydroquinone was added to it. This portion of the mixture was analyzed by SEC directly. The rest of the mixture was poured into stirring hexane, and brown precipitate was separated by centrifugation. The polymer was reprecipitated from either THF or chloroform into hexane to remove residual oDCB and dried under vacuum.

PS/DMA and PMMA/DMA. C_{60} (25 mg, 3.5×10^{-5} mol) was dissolved in 4.0 mL of oDCB, and the solution was stirred under nitrogen for 10 min. DMA (72 mg, 3.5×10^{-4} mol) was added and the mixture stirred for 30 min. A solution of 1.0 mL of oDCB, 28 mg (1.7×10^{-4} mol) of AIBN, and 2.5 g of either styrene or MMA was added and the mixture stirred for 30 min. The mixture was heated to 60 °C for 72 h. After cooling, the solution was added dropwise to stirring hexane, and precipitated brown solid was isolated by centrifugation. The solid was precipitated twice more from THF into hexane, and dried in vacuum at 50 °C to give 1.1 g (47%) of polystyrene/C_{60} or 1.8 g (77%) of PMMA/C_{60}.

Fractionation of Polymers in Methanol. This example describes higher AIBN/C_{60}, mole ratios, more dilute solutions, and precipitation of the products into methanol. Solutions of 11.7 mL of MMA in 111 mL of oDCB and 84 mg (0.117 mmol, 0.77 wt %) of C_{60} in 13.5 mL of oDCB were stirred for 60 min, combined, and stirred under nitrogen for 30 min. A solution of 209 mg (1.28 mmol) of AIBN (AIBN/C_{60} = 11) in 7.5 mL of oDCB was added. The combined solution was purged with nitrogen for 20 min and heated to 60 °C. Aliquots of 48 mL were removed after 5, 10, and 48 h, precipitated into 1000 mL of methanol, and centrifuged. The solid was dissolved into 20 mL of chloroform, reprecipitated into methanol, centrifuged, and dried under vacuum at room temperature. More polymer was recovered by evaporation of the methanol solutions and drying the combined residue under vacuum.

A nearly identical polymerization of styrene used 61.4 mg (0.0852 mmol, 0.53 wt %) of C_{60} in 10 mL of oDCB, 11.5 g of styrene, and 209 mg of AIBN (AIBN/C_{60} = 15).

SEC Analyses. The multidetector size exclusion chromatographic system was described earlier.[24] SEC analysis in THF used three 7.5 mm × 300 mm PLgel mixed-C columns (Polymer Laboratories). Separations in toluene containing 0.1% v/v acetic acid were on three 7.5 mm × 300 mm PLgel mixed-B columns. Fullerenes were detected by UV absorbance at 330 nm, the mass of the polymer by differential refractive index (DRI), and specific solution viscosity by differential viscometry (DV). Detectors were connected in series in the order UV, DV, and DRI. Intrinsic viscosities ($[\eta]$, dL g^{-1}) were calculated at each retention volume from measured viscosities and mass concentrations, and absolute molecular weights were calculated from a universal calibration curve. Whole polymer intrinsic viscosities and molecular weight averages were calculated in the normal manner by summation of values across the molecular size distribution. Reaction mixtures (oDCB solutions, 0.5 g) were diluted into 5 mL of THF or toluene. In some cases excess AIBN precipitated as white needles, or C_{60}-rich material precipitated as a black solid. All samples were filtered through 0.5 μm Teflon membranes before injection. Most samples did not appear cloudy and gave good mass balance between the amount of sample injected and the integrated area of the DRI chromatogram. Only polystyrene equivalent molecular weights of the THF-soluble fractions from the DRI response could be calculated because the concentrations of the diluted reaction mixtures were not known accurately.

Fullerene contents of polymers were estimated from SEC peak areas at 330 nm and sample weights injected. Three 85−92% conversion PMMA/C_{60} samples (two from this work and one from previous work[20]) made from 1.00 wt % C_{60} were used as standards to determine (peak area)/(mg/mL) with an average deviation of 4%. The analyses assume that all of the fullerene polymers have the same extinction coefficient at 330 nm.

UV molar chromatograms were created by converting absorbance to molar concentration and plotting against retention volume. Similarly mass molar chromatograms were created by converting DRI response to molar concentration using the absolute molecular weights calculated from intrinsic viscosity and universal calibration. Comparison of the UV with the mass molar chromatogram gives the average number of fullerene units per macromolecule across the entire molecular weight distribution.[20]

Results

Compositions of Low-Conversion Polymers. With the aim of learning how polymerization of C_{60} with vinyl monomers initiated by AIBN begins, polymerizations were carried out for 30 and 120 min at 75 °C in oDCB solutions using 5 mol of AIBN/mol of C_{60} and 1 wt %

Table 2. Compositions of Polystyrene/C_{60} and PMMA/C_{60} Samples

sample[a]	%C	%H	%N	%O	wt % C_{60}	mol of monomer/ mol of fullerene	mol of C_4H_6N/ mol of fullerene
PS30C	87.99	2.21	0.81	7.02	62.8	2.7	0.66
PS30C[b]					73.3	1.2	0.57
PS120B	86.51	4.51	1.65	5.95	35.3	9.7	2.4
PS120B[b]					44.1	6.2	1.9
PMMA30B	63.83	6.95	0.49	(26.96)[c]	12.1	50	2.1
PMMA120B	63.50	7.32	0.58	(28.18)[c]	8.5	75	3.5

[a] Samples named with suffix B were insoluble in hexane and soluble in THF. Samples named with suffix C were insoluble in both hexane and THF. [b] Elemental analyses were normalized to 100% assuming all oxygen was from water. [c] %O calculated from %H assuming all H came from C_4H_6N end groups and $C_4H_8O_2$ monomer.

C_{60} relative to monomer, and the polymers were isolated by precipitation into hexane. The supernatant hexane solutions from polymers isolated after 30 min of reaction of styrene and after both 30 and 120 min of reaction of MMA were purple due to unreacted C_{60}. The hexane solution from 120 min of polymerization of styrene was brown due to low molar mass C_{60} adducts. The precipitates were fractionated by washing with THF. The fractions soluble in THF had high polystyrene or PMMA content, whereas the insoluble fractions were rich in fullerene. C_{60} itself is completely insoluble in THF. The major fractions isolated are described in the footnotes of Table 1.

Elemental analyses of the major fractions of the precipitated polymers are reported in Table 2. Direct oxygen analyses found 6−7% oxygen in the polystyrene/C_{60} samples. The oxygen could be due to adsorbed water or to oxidation of the fullerene by adventitious dioxygen, which is difficult to remove from the reaction mixtures.[25] Approximate relative molar amounts of fullerene, 2-cyano-2-propyl (C_4H_6N) groups from AIBN, and monomer units in the polymers were calculated from the elemental analyses using eqs 1−7, which assume that all N

$$\%\text{H from } C_4H_6N = \%N_{obs}\,(6/14) \quad (1)$$

$$\%\text{H from monomer} = \%H_{obs} - \%\text{H from } C_4H_6N \quad (2)$$

$$\%\text{C from monomer} = \%\text{H from monomer}\,(96/8)\ (\text{for styrene}) \quad (3a)$$

$$\%\text{C from monomer} = \%\text{H from monomer}\,(60/8)\ (\text{for MMA}) \quad (3b)$$

$$\%\text{C from } C_{60} = \%C_{obs} - \%\text{C from } C_4H_6N - \%\text{C from monomer} \quad (4)$$

$$\text{mmol of } C_4H_6N/\text{g of sample} = \%N_{obs}/1.4 \quad (5)$$

$$\text{mmol of monomer/g of sample} = \%\text{H from monomer}/0.8 \quad (6)$$

$$\text{mmol of } C_{60}/\text{g of sample} = \%\text{C from } C_{60}/72 \quad (7)$$

came from C_4H_6N groups, and all H came from C_4H_6N groups and monomer units. The results are reported in Table 2 along with the results of similar calculations that assume all oxygen in the polystyrene/C_{60} samples came from water. Although the calculated data may contain large propagated errors, they indicate that the degree of polymerization of styrene after 120 min is <10 and that of MMA after 30−120 min is 50−75. In a quantitative ^{13}C NMR spectrum of PS120B the relative areas of (a) the 135−160 ppm band for fullerene aromatic carbons and substituted aromatic polystyrene carbons and (b) the 120−135 ppm bands for protonated aromatic polystyrene and cyano carbons indicate 11 polystyrene repeat units per fullerene, in reasonable agreement with the 6−10 styrene units per C_{60} calculated from elemental analyses.

After 30 min the major part of the reaction product from styrene contained more fullerene units than 2-cyano-2-propyl groups and was insoluble in THF, whereas the major fractions of products from MMA after 30 min and after 120 min, and from styrene after 120 min, were soluble in THF and contained more 2-cyano-2-propyl groups than fullerene units. From an estimated rate constant for decomposition of AIBN of 6.9×10^{-5} s^{-1} at 75 °C,[26] 12% of the AIBN decomposed in 30 min, giving 1.2 mol of 2-cyano-2-propyl radicals/mol of C_{60}, and 39% of the AIBN decomposed in 120 min, giving 3.9 mol of 2-cyano-2-propyl radicals/mol of C_{60}. Not all of the 2-cyano-2-propyl radicals react with monomer or with C_{60}; some combine or disproportionate.

Molecular Weight Distributions. Both the unfractionated reaction mixtures and the precipitated polymers were analyzed by SEC. Samples that were soluble in THF were analyzed by DRI for mass, UV at 330 nm for fullerenes, and DV for determination of absolute molecular weights via universal calibration. Although C_{60} is completely insoluble in pure THF, no precipitates formed when 0.5 mL of reaction mixtures was diluted into 5.0 mL of THF. Thus, C_{60} and all of the products were soluble in 91:9 THF/oDCB. Some of the reaction mixtures also were analyzed after dilution in toluene. Molecular weights relative to linear polystyrene standards (P_n and P_w) are reported for reaction mixtures in Table 3, and absolute molecular weights (M_n and M_w) are reported for samples that could be weighed and dissolved in THF.

When the oDCB reaction mixture PS30A from 30 min of reaction of styrene was added to toluene, AIBN precipitated as white needles. PS30A was completely soluble in 91:9 THF/oDCB. SEC analyses in both toluene and THF showed no signal from the viscosity detector and $P_w < 1000$ from the DRI and UV detectors. The UV detector showed peaks for unreacted C_{60} and several low molar mass compounds.

The reaction mixture PS120A from 120 min reaction of styrene gave slightly turbid solutions after addition to THF or toluene. (Some crystalline AIBN was filtered out of the toluene solution.) As shown in Figure 1, the chromatograms had no viscosity signal, the UV and DRI signals were multimodal, and the DRI signal gave $P_w = 8800$. However, the major fraction PS120B precipitated from hexane and redissolved in THF gave the multimodal SEC in Figure 2 with a weak viscosity signal, and a very broad absolute molecular weight distribution with $M_n = 6400$ and $M_w = 144\,000$. These chromatograms, and the 35−44 wt % of C_{60} from elemental analysis in Table 2, show that the polystyrene/C_{60} after 120 min contained much polymerized or clustered C_{60} having very low intrinsic viscosity and high UV absorbance.

In contrast to the multimodal molecular weight distributions of the polystyrene/C_{60}, the PMMA/C_{60} samples had monomodal distributions. As shown in Figure 3, the maximum DV response occurred at lower retention volume than the DRI and UV responses as

Table 3. SEC Analyses of Polymers Isolated by Precipitation into Hexane[a]

sample[b]	solvent	P_n[c]	P_w[c]	M_n[d]	M_w[d]	comments
PS30A	THF	370	850			no viscosity signal
PS120A	THF	2800	8800			slightly turbid, DRI and UV trimodal, no viscosity signal
PS 120B	THF	3840	19200	6400	128000	DRI and UV prepeak, trimodal, $[\eta] = 0.042$[e]
PMMA30A	THF	4090	6790			monomodal
PMMA30B	THF	6140	10600	8610	15800	monomodal, $[\eta] = 0.067$[e]
PMMA60*a*	toluene	3710	7620			
PMMA60*b*	THF	3520	6920	4770	6950	
PMMA120A	THF	3940	8030			monomodal
PMMA120B	THF	4620	8840	7030	11400	$[\eta] = 0.068$[e]
PMMA120*a*	toluene	5410	10500			
PMMA120*b*	THF	5510	10650	7930	12100	

[a] See Table 1 for sample identification. [b] Samples ending in A and *a* are original reaction mixtures; those ending in B and *b* are products precipitated from hexane and soluble in THF. [c] Molecular weights relative to polystyrene standards. [d] Absolute molecular weights. [e] Intrinsic viscosity in dL g^{-1}.

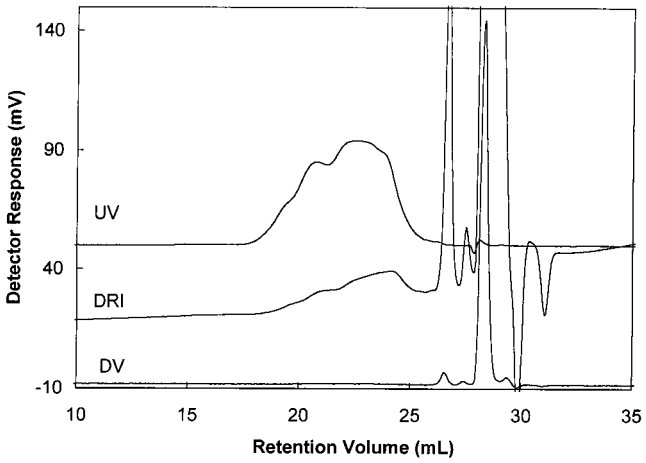


Figure 1. SEC chromatogram of reaction mixture PS120A in THF.

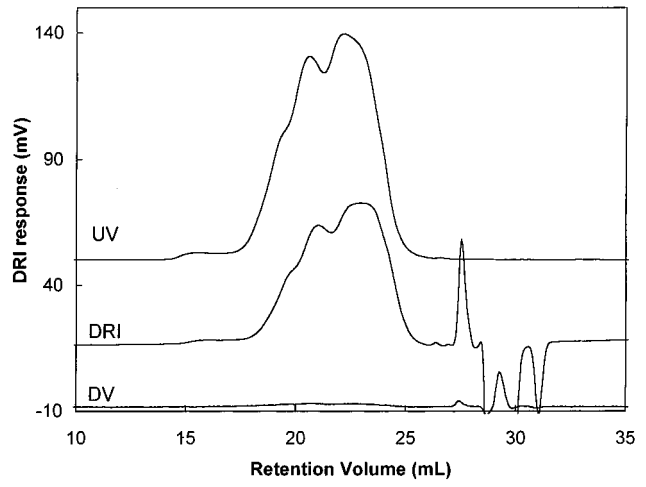


Figure 2. SEC chromatogram of hexane-insoluble polymer PS120B in THF.

expected because DV is more sensitive to high-mass than to low-mass components. Samples PMMA30B and PMMA120B isolated in 1% and 6% yields after 30 and 120 min, respectively, had similar absolute molecular weights, which were significantly higher than the molecular weights relative to polystyrene standards (*P*). Therefore, the polymers had branched structures, as observed before for higher conversion PMMA/C_{60} samples.[20]

The PMMA/C_{60} experiments were repeated to test their reproducibility and to determine whether hexane precipitations fractionated the polymers. These polymer

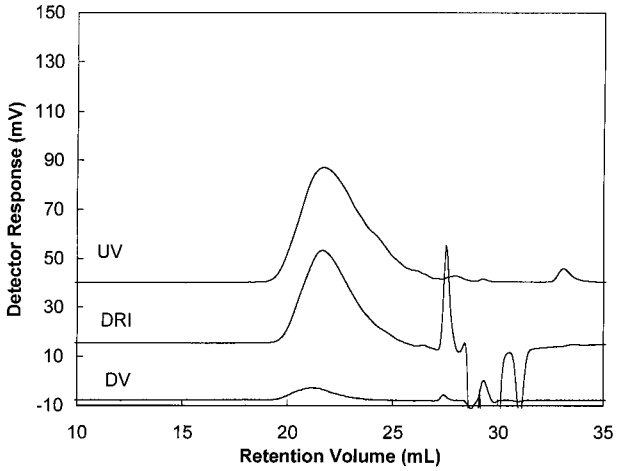


Figure 3. SEC chromatogram of PMMA120.

samples are listed in Table 3 with the suffixes *a* for reaction mixtures analyzed directly in toluene and *b* for samples isolated by precipitation into hexane. The key results are as follows. (a) Duplicate experiments 120A and 120*a*, and also 120B and 120*b*, gave *P* values differing by about 20%. This is reasonable agreement for completely independent preparations. (b) The *P* values for original reaction mixtures 60*a* and 120*a* and those for the precipitated polymers 60*b* and 120*b* agree within 10%. Therefore, hexane precipitation does not fractionate the samples. (c) The *P* values are only slightly less than the *M* values of samples 60*b* and 120*b*, indicating little branching in the structures. (d) The greater UV signal relative to the DRI signal at high retention volume in the chromatograms of sample PMMA60*b* shows that the fullerene content was greater at the lower end of the molecular weight distribution.

In separate experiments, polymerization mixtures of styrene and of MMA containing 1 wt % C_{60} and a 5:1 mole ratio of AIBN/C_{60} were analyzed without isolation of products by adding the mixtures directly to toluene containing 0.2% acetic acid. All samples were completely soluble. Figure 4 shows disappearance of C_{60} from the styrene mixture, appearance of peaks from molecules of intermediate size, and finally appearance of polymer over 120 min. The polymer peak was never monomodal. The spacing between the peaks in Figure 4 is approximately linear, which implies that the hydrodynamic volume of the fundamental units of the polymers increases monotonically (doubles, triples, etc.). This normally corresponds to an exponential increase in molar mass. Figure 5 shows the appearance of similar peaks of intermediate molecular weight in the MMA

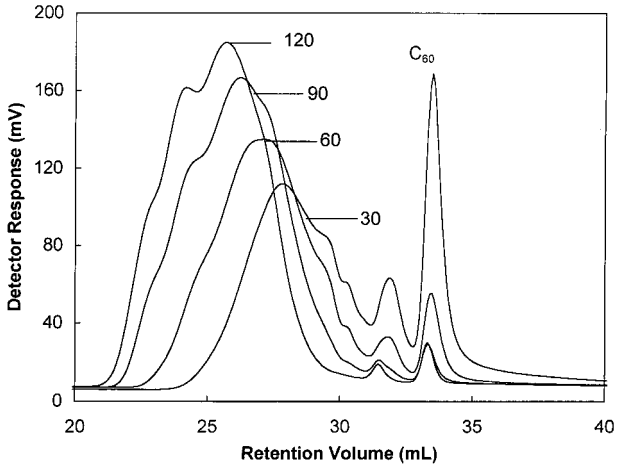


Figure 4. SEC chromatograms detected by UV at 330 nm in toluene of reaction mixtures of AIBN, styrene, and C_{60} in toluene after reaction times of 30−120 min at 75 °C.

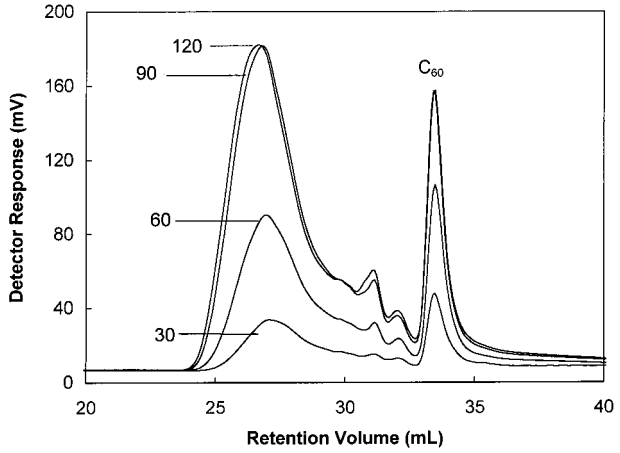


Figure 5. SEC chromatograms detected by UV at 330 nm of reaction mixtures of AIBN, MMA, and C_{60} in toluene after reaction times of 30−120 min at 75 °C.

reaction mixture, earlier formation of polymer, and almost no molecular weight increase over 60−120 min. Compared with the polystyrene/C_{60} chromatograms of Figure 4, the PMMA chromatograms are monomodal, and have much lower molecular weight.

Molar chromatograms are shown in Figure 6 for samples PMMA30B and PMMA120B. The values for weight percent C_{60} in Table 2 were used to calculate molar concentrations of fullerene, and the absolute molecular weights were used to calculate molar concentrations of polymer. The results reveal >10 to <1 fullerene units per macromolecule from high to low molecular weight in the sample isolated after 30 min and 10 to <1 fullerene units per macromolecule in the sample isolated after 120 min. This proves that structures containing more than one fullerene unit form early in the MMA polymerizations as well as in the styrene polymerizations. Previously we found an average of no more than one fullerene unit per macromolecule in PMMA/C_{60} across the entire molecular weight distribution after higher conversion.[20] The low average could have been due to mixtures of linear polymer with polymer containing more than one fullerene unit.

Homopolymerization of C_{60}. Under standard concentrations, solutions of AIBN and C_{60} in a 5:1 mole ratio in oDCB in the absence of monomer were heated to 75 °C for varied times, cooled, and stabilized with

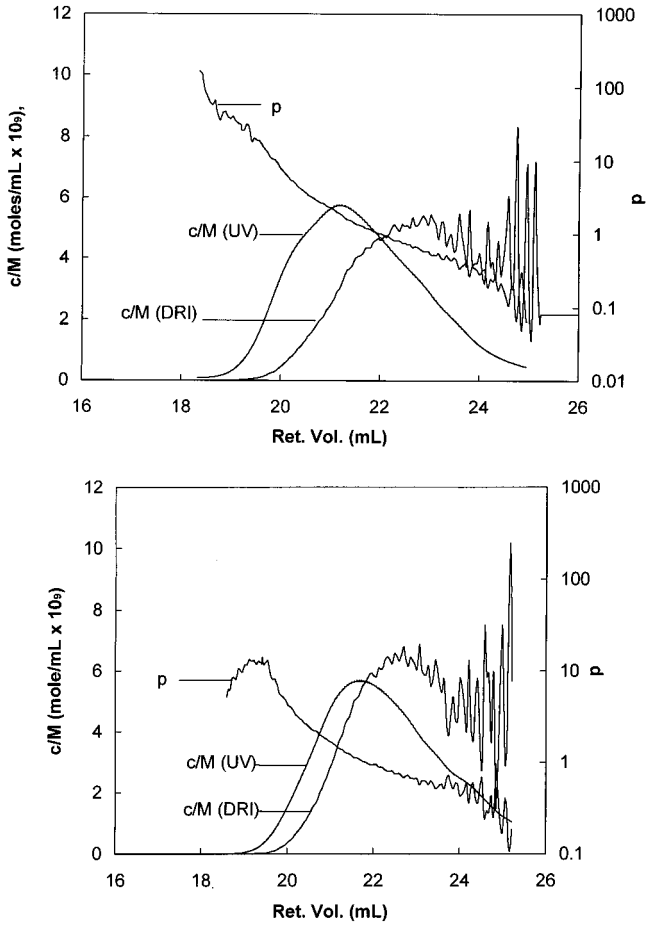


Figure 6. Molar chromatograms of fullerene distribution and mass distribution, and number of fullerene units per macromolecule (*P*) of low-conversion samples PMMA30B containing 10.7 wt % C_{60} (A, top) and PMMA120B containing 8.5 wt % C_{60} (B, bottom).

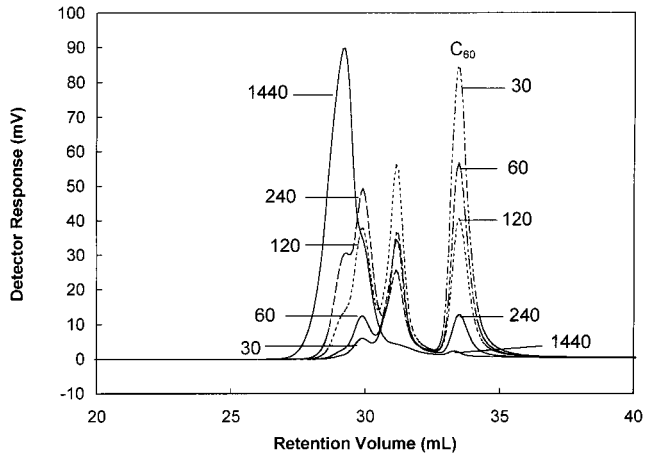


Figure 7. SEC chromatograms detected by UV at 330 nm in toluene of products from reaction of AIBN with C_{60} but no monomer. The times are in minutes at 75 °C.

hydroquinone. The samples were added to toluene containing 0.2% acetic acid and analyzed by SEC. The progression of chromatograms in Figure 7 shows the disappearance of C_{60} over 240 min, appearance of low molar mass adducts at 30−240 min, and finally formation of polymer over 24 h. No absolute molecular weights could be calculated because of weak DV signals. This indicates compact structures in toluene. Among the peaks between the polymer and the starting C_{60} are the

Table 4. SEC Analyses of High-Conversion Polymers

sample	solvent	P_n	P_w	M_n	M_w	comments[c]
PS[a]	THF			34000	54100	
PS-DMA[b]	THF	44 700	98 600	47 800	144 000	monomodal, $[\eta] = 0.356$
PS-DMA[b]	toluene	43 700	98 000	58 900	152 000	$[\eta] = 0.308$
PMMA[a]	THF			55 500	99 300	
PMMA1440*a*	toluene	32 500	50 800			
PMMA1440*b*	THF	33 300	50 900	35 100	50 500	
PMMA-DMA[b]	THF	30 700	50 100	39 900	60 100	monomodal, $[\eta] = 0.228$

[a] Polymerized for 10 h in the absence of C_{60} under otherwise the same conditions as the samples in Tables 1 and 3. [b] Polymerized at 60 °C for 72 h in the presence of a 10:1 mole ratio of DMA/C_{60} as described in the Experimental Section. [c] Intrinsic viscosity in dL g^{-1}.

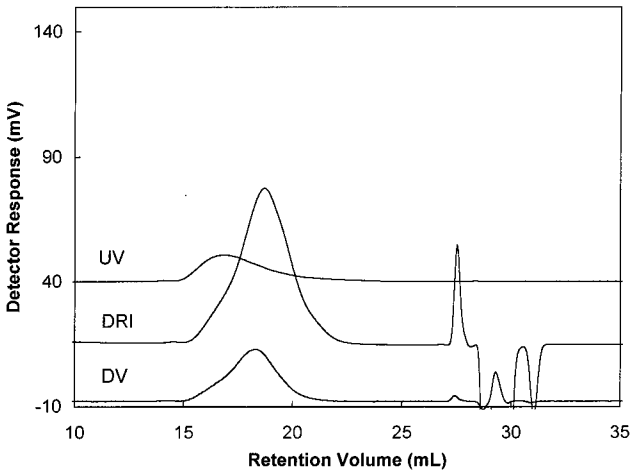
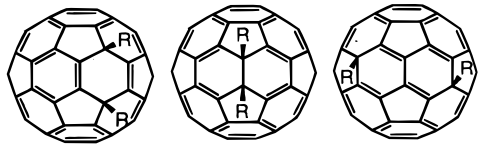


Figure 8. SEC chromatograms of PS-DMA. For sample properties see Table 4.

isomeric di(2-cyano-2-propyl)dihydro[60]fullerenes **1**−**3** that we isolated and characterized recently.[27] This experiment proves that C_{60} homopolymerizes with AIBN initiation to a product of low intrinsic viscosity. C_{60} also homopolymerizes with initiation by benzoyl peroxide.[17]



R = $C(CH_3)_2CN$ **1** **2** **3**

R = $C(CH_3)_2CO_2CH_3$ **4** **5**

High-Conversion Polymers. Table 4 reports polystyrene and PMMA prepared in the absence of C_{60}, high-conversion polystyrene/C_{60} and PMMA/C_{60} prepared both by our standard method and also in the presence of added 9,10-dimethylanthracene (DMA). The homopolystyrene had a narrower molecular weight distribution and had lower M_w than the polystyrene/C_{60}. On the other hand, homo-PMMA had higher *M* values than PMMA/C_{60}. The purpose of DMA, which forms multiple Diels−Alder adducts with C_{60},[28] was to reduce the rate of addition of radicals to the fullerenes. However, at 60 °C in oDCB, the DMA had little effect on the absolute molecular weights, as shown in Table 4 and Figure 8.

Sonication of Solutions before Polymerization. Previously polymerizations of MMA with C_{60} after 2−16 h gave branched PMMA/C_{60} containing an average of no more than one fullerene unit per macromolecule over the entire molecular weight distribution,[20] whereas polystyrene/C_{60} had many fullerene units per macromolecule at the high end of the molecular weight distribution.[20] In the earlier work, mixtures of C_{60} in oDCB were sonicated to speed dissolution of C_{60}, and air was not purged from the solutions until after the monomer was added. Suspecting that C_{60} or clusters of fullerenes might oxidize in air,[25] we analyzed a C_{60} solution by HPLC after sonication, but found only unchanged C_{60}. The polymerization experiments were repeated by stirring, and by sonicating, the C_{60} in oDCB under nitrogen before adding initiator. After polymerization for varied times the reaction mixtures were poured into stirring methanol, a procedure that partially fractionates the PMMA, as described later. Table 5 reports that the higher polystyrene equivalent molecular weight (*P*) fractions B and the lower *P* fractions C isolated after 60 and 120 min had absolute molecular weight (*M*) values significantly higher than *P* values, indicating that the PMMA/C_{60} isolated after 60−120 min had branched structures. The high-conversion samples SPMMA1440A and SPMMA1440MB, which contained much linear PMMA, had nearly equal *P* values, and SPMMA1440MB had nearly equal *P* and *M* values. Thus, after sonicating under nitrogen, the low-conversion PMMA/C_{60} had branched structures, but the large amount of homopolymer in the high-conversion samples prevented detection of the branched components.

Table 5. Effect of Sonication of C_{60} Solutions on PMMA Molecular Weight[a]

sample (atmosphere during sonication)[b]	yield (%)	wt % C_{60}	P_n	P_w	M_n	M_w
SPMMA60A (N_2)			4115	8290		
SPMMA60MB (N_2)	0.7	7.0	8670	19050	14150	21450
SPMMA60MC (N_2)	5.5	12	2380	5670	4930	8585
SPMMA120A (N_2)			10500	19100		
SPMMA120MB (N_2)	11	3.7	17600	23750	21400	26500
SPMMA120MC (N_2)	16	7	2885	7415	4285	9720
SPMMA1440A (N_2)			24350	42650		
SPMMA1440MB (N_2)	60	1.02	30850	45150	29950	44150
SPMMA60 (air)	4	11	3165	6175	5200	8260
SPMMA120 (air)	10	8	4875	9485	5760	12800
SPMMA120[c] (air)	12		9360	15600	10070	18100
SPMMA1440 (air)	84	1.1	22250	35250	34300	51800
SPMMA960[c] (air)	97	1.0	26400	44800	33800	54900

[a] All solutions were prepared by sonication of C_{60} in oDCB for 1 h. Polymerizations were carried out under nitrogen with 1 wt % C_{60} relative to monomer and an AIBN/C_{60} mole ratio of 5:1 in oDCB solution at 75 °C. [b] Numbers in sample names refer to minutes of reaction time, A refers to original reaction mixtures, MB refers to samples insoluble in methanol, and MC refers to the methanol-soluble fractions. The last five samples were isolated by precipitation into hexane. [c] Data from ref 20.

The experiments were repeated by dissolving C_{60} in oDCB by sonication in air as before,[20] and the samples were recovered by precipitation into hexane, which does not fractionate the PMMA, to give the last five samples reported in Table 5. The *P* values from the original

reaction mixtures (not shown in Table 5) were the same as the *P* values from these precipitated polymers, and similar to those of the hexane-precipitated samples reported in Table 3. After sonication of the C_{60}/oDCB solution in air and polymerization under nitrogen, the *M* values exceeded the *P* values, even after 24 h of reaction, confirming that these PMMA/C_{60} samples have branched structures. In contrast, polymerizations in which the C_{60} was dissolved in oDCB by stirring under nitrogen, such as the samples reported in Table 3, gave *M* values only slightly larger than *P* values, indicating much less branched PMMA. Thus, sonicating the C_{60} solution in air before polymerization under nitrogen led to more highly branched PMMA/C_{60} than sonicating or stirring the C_{60}/oDCB solution in nitrogen. Most likely sonication in air either autoxidizes some of the C_{60} or makes it aggregate more than in the absence of dioxygen.

Fractionation of PMMA/C_{60} by Precipitation into Methanol. Methanol precipitated almost all polystyrene/C_{60}, but sizeable amounts of lower molecular weight PMMA/C_{60} did not precipitate. Amounts of recovered methanol-insoluble and methanol-soluble/hexane-insoluble materials, and SEC analyses of both the isolated solids and the original reaction mixtures, are in Table 5. The precipitated samples SPMMA60MB, -120MB, and -1440MB from 60, 120, and 1440 min of reaction were insoluble in methanol and had polystyrene equivalent molecular weight values (*P*) greater than those of the original reaction mixtures SPMMA60A, -120A, and -1440A. The methanol-soluble fractions SPMMA60MC and -120MC had *P* values less than those of the original reaction mixtures. Thus, methanol selectively dissolved lower molecular weight parts of the PMMA/C_{60}. After 24 h of reaction, almost no methanol-soluble PMMA/C_{60} remained, and the precipitated sample B had polystyrene equivalent and absolute molecular weights similar to those of the original reaction mixture A.

Polymerizations at 60 °C with More AIBN/C_{60}. Stewart and Imrie reported copolymerizations of C_{60} with styrene and of C_{60} with MMA initiated by AIBN in benzene solutions at 60 °C, using more dilute solutions and larger AIBN/C_{60} mole ratios than ours, and concluded that the monomers polymerized without a significant induction period but at slower rates than in the absence of C_{60}.[29,30] We carried out polymerizations under their conditions, except using oDCB instead of benzene as solvent, and precipitated the reaction mixtures into methanol as they did. Yields and absolute molecular weights of the methanol-soluble and methanol-insoluble materials from the DRI and DV chromatograms are reported in Table 6. The methanol-soluble PMMA/C_{60} in all samples had $M_w = 10\,000$, and the molecular weights of the methanol-insoluble PMMA/C_{60} increased with time. Plots of log *M* vs retention volume of the three methanol-insoluble polymers were nearly coincident with that for linear PMMA, which indicates that the polymers were not significantly branched. The UV chromatograms of the methanol-insoluble PMMA/C_{60} samples were similar to those of Figure 5. After 5 h (sample PMMA5 in Table 6) there were unreacted C_{60}, low molecular weight adducts of C_{60}, polymer, and a small amount of ultrahigh molecular weight polymer (detected as a prepeak in the chromatogram). After 10 h (PMMA10), the chromatogram showed low molecular weight adducts and polymer but no prepeak. After 48 h (PMMA48) there was only polymer. The prepeak that appeared in the UV but not in the DRI chromatogram of PMMA5 must be due to clusters of fullerenes that break down as the reaction proceeds further. The main polymer components of PMMA5 and PMMA10 had slightly smaller retention volumes in the DRI than in UV chromatograms, which indicates higher fullerene content in the lower end of the molecular weight distribution, whereas the fullerene was more uniformly distributed in the PMMA48. The UV chromatogram of the methanol-soluble fraction after 5 h also showed unreacted C_{60} and low molar mass fullerenes in addition to polymer. Since C_{60} is totally insoluble in methanol, its presence in the soluble fraction was due to solubility in a 48:1000 mixture of oDCB/methanol. Low molar mass adducts of C_{60} also remained in the methanol-soluble polymers after 10 and 48 h.

Table 6. Polymers from Greater AIBN/C_{60} at 60 °C[a]

	methanol-insoluble				methanol-soluble			
sample	yield (%)	wt % C_{60}	M_n	M_w	yield (%)	wt % C_{60}	M_n	M_w
PMMA5	0.4	10	24350	27350	6.5	8	5745	10135
PMMA10	4.9	8	24500	31850	8.8	2.6	8013	10400
PMMA48	38	1.4	39675	53250	*c*	0.5	7438	10050
PS5	0.4	43	1478[d]	5465[d]	1.0	29	509	2285
PS10	0.4	32	5515	7740	1.4	29	1620	3245
PS48	38	1.6	12075	17400	2.1	5.3	789	3430

[a] See Fractionation of Polymers into Methanol in the Experimental Section for polymerization and isolation procedures. [b] Numbers in sample names are hours reacted. [c] Not determined. [d] Both peaks of a bimodal distribution were included in the calculations.

Table 6 also shows the molecular weights of polystyrene/C_{60} samples that are similar to those of Stewart and Imrie.[29,30] Both the methanol-soluble and the methanol-insoluble samples after 5 and 10 h had greater molar mass than linear polystyrene of equal retention volume, and therefore are branched. The 48 h sample behaved as a linear polymer by SEC.

Residual Radicals in the Polymers. Stewart and Imrie reported that their polystyrene/C_{60} gave a strong ESR signal of a fullerene radical in benzene solution before isolation of the polymer.[29] The signal decayed with time, especially when exposed to air. Some ESR signal remained even after precipitation and drying of the polymer. In contrast, they detected no fullerene ESR signal during polymerization of MMA and C_{60} in benzene solution.[30] We found ESR spectra of fullerene radicals from all five of the solid polystyrene/C_{60} and PMMA/C_{60} samples (ones listed in Tables 5 and 6) that we tested. Low-conversion PMMA120B gave about 5 times stronger a signal than PMMA30B, and high-conversion PMMA1440*b* was still weaker. The polystyrene/C_{60} sample PS48 also gave a strong ESR signal, whereas PS120B was weaker. Thus, fullerene radicals remained in the solid polymer samples after precipitation and drying in air.

Locations of the End Groups. Syntheses of the PS120, PMMA30, and PMMA120 samples were repeated using AIBN 97% ^{13}C-enriched at the central carbon atom under conditions listed in Table 1. The ^{1}H and ^{13}C NMR spectra of PS 120-^{13}C (Figure 9A) had much broader lines than those of linear polystyrene. The ^{13}C-enriched NMR signals in the PS120-^{13}C spectrum were assigned from HMBC spectra which correlated polystyrene CH_2 groups with the signal at 32 ppm, but not with the signal at 41 ppm. The assignments are

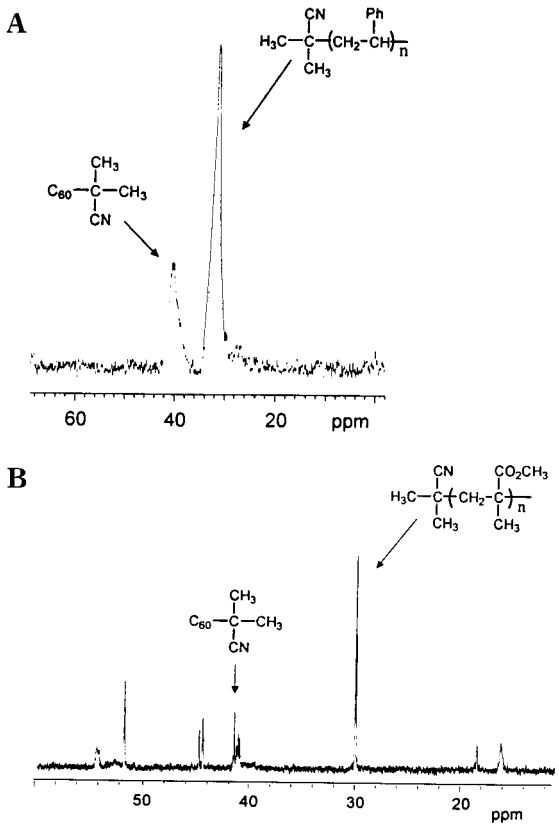


Figure 9. (A, top) ^{13}C NMR spectrum of PS120-^{13}C. The aliphatic polystyrene signals at natural abundance contribute <10% of the 40 ppm peak. (B, bottom) ^{13}C NMR spectrum of PMMA120-^{13}C.

supported by a 40 ppm signal for the quaternary carbons of three different isomers of di(2-cyano-2-propyl)dihydro-[60]fullerene (**1**−**3**),[27] and 32 ppm signals for 2-cyano-2-propyl end groups of styrene oligomers.[31−34] The relative area of the signals at 32 and 41 ppm was 74:26. Correction for a small contribution of the polymer methine carbon signal at 32 ppm gave a 72:28 ratio of end groups on polystyrene to end groups on fullerene.

The ^{1}H and ^{13}C NMR spectra of PMMA30-^{13}C and PMMA120-^{13}C had line widths similar to those of linear PMMA. The prominent natural abundance signals in Figure 9B indicate a much larger amount of PMMA in PMMA120-^{13}C than of polystyrene in PS120-^{13}C (Figure 9A). The broad fullerene band at 135−160 ppm was not apparent in the spectrum of PMMA120-^{13}C. An HMBC spectrum correlated the signals at 30 ppm with signals of PMMA end groups. The signals at 42 ppm are due to 2-cyano-2-propyl groups bound directly to fullerene. The relative areas of the 30 and 42 ppm signals indicate a 62:38 ratio of end groups on PMMA to end groups on fullerene. By the same method the spectrum of PMMA30-^{13}C showed a 61:39 ratio of end groups. Thus, the fraction of end groups on PMMA did not change between 30 min and 120 min.

Stability of C_{60} Adducts under Polymerization Conditions. If bond formation between polymer radicals and fullerene, or between 2-cyano-2-propyl radicals and fullerene, is reversible, the polymeric products and the isomeric di(2-cyano-2-propyl)-l,*x*-dihydro[60]fullerenes **1**−**3** should initiate polymerization of more monomer as in living radical polymerizations.[35] To test this possibility, in separate experiments the low molar mass mixture of 1,2- and 1,4-di(2-cyano-2-propyl)-l,*x*-dihydro-[60]fullerenes (**1** and **2**), the 1,16-isomer of these cyanopropyl compounds (**3**), and the 1,4- and 1,16-isomers of di(2-carbomethoxy-2-propyl)-1,*x*- dihydro[60]fullerene (**4** and **5**) were mixed with 700 molar equivalents of styrene or MMA in oDCB-d_4, degassed, sealed under vacuum in NMR tubes, and heated at 75 °C for 24 h while protected from light. The ^{1}H NMR spectra showed no evidence of polymer formation. Similar experiments using a mixture of more highly substituted fullerenes from reaction of C_{60} with 5 molar equivalents of AIBN also showed no polystyrene or PMMA in the ^{1}H NMR spectra after 72 h at 75 °C. Thus, the AIBN/C_{60} adducts **1**−**3** and the analogous methyl esters **4** and **5** do not initiate the polymerizations. In a ^{13}C-enriched version of this experiment, a mixture of 2-cyano-2-propyl-α-^{13}C adducts of C_{60} was prepared by heating 2.5 molar equivalents of AIBN-α-^{13}C with C_{60} in oDCB for 72 h, and then 2.5 molar equivalents of natural abundance AIBN and 100 g of MMA/g of C_{60} were added and heated to 75 °C for 120 min so that the total amounts of materials used were the same as in other MMA polymerizations. The ^{13}C NMR spectrum of the product recovered from precipitation into hexane had the usual peaks at 41 ppm for the enriched carbon bound to fullerene, and the area of the peak at 31 ppm for end groups bound to PMMA was less than 3% as large, indicating no significant amount of ^{13}C end groups on PMMA. Similar experiments were carried out by precipitating polystyrene/C_{60} and PMMA/C_{60} samples after various reaction times and reheating them with more monomer in oDCB at 75 °C. No increase in molecular weight of the polymer was observed in any such experiment. Thus, the fullerene radicals in the samples do not initiate further polymerization, and alkyl−fullerene bonds do not dissociate to form 2-cyano-2-propyl, polystyryl, and PMMA radicals, which also would lead to further polymerization.

To test whether sonication of C_{60} solution affected the relative rates of addition of 2-cyano-2-propyl radicals to C_{60} and to monomer, the AIBN-^{13}C was heated for 120 min at 75 °C with MMA and the usual amount of C_{60} that had been sonicated in oDCB. The PMMA/C_{60} product again contained a 61:39 ratio of end groups on PMMA vs C_{60}. Therefore, sonication did not affect the reactivity of the fullerene with the 2-cyano-2-propyl radical.

Discussion

A mechanism of radical copolymerization of C_{60} with styrene and with MMA should explain the compositions and structures of the low- and high-conversion polymers. Those key results are as follows.

(1) Molar size exclusion chromatograms from UV detection of fullerenes, DRI detection of the mass of the polymer, and DV detection of the intrinsic viscosity of the polymer show that both polystyrene/C_{60} and PMMA/C_{60} products isolated after low conversion of monomer contain many fullerenes per molecule.

(2) Lower intrinsic viscosity and higher absolute molecular weight of the fullerene-containing polymers compared with linear polystyrenes at equal retention time show that the polymer structures are branched.[20]

(3) Elemental analyses, NMR spectra, and SEC show that the C_{60} content is higher and the polymer chain lengths are shorter in the low-conversion polystyrene/C_{60} than in the low-conversion PMMA/C_{60}.

(4) C_{60} itself polymerizes when initiated by AIBN. After low conversion 1,2-, 1,4-, and 1,16-di(2-cyano-2-

	estimated rate constants	
I(AIBN) → 2 R• ($Me_2\dot{C}CN$)	6.9×10^{-5} s^{-1}	(8)
R• + M → RM• (M = styrene or MMA)	10^4 M^{-1} s^{-1}	(9)
$R(M)_n$• + M → $R(M)_{n+1}$•	10^3 M^{-1} s^{-1}	(10)
2 $R(M)_n$• → P (P = linear polymer)	$2\text{-}8 \times 10^7$ M^{-1} s^{-1}	(11)
R• + C_{60} → RC_{60}•	10^9 M^{-1} s^{-1}	(12)
$R(M)_n$• + C_{60} → $R(M)_nC_{60}$•	10^9 M^{-1} s^{-1}	(13)
R• + RC_{60}• → R_2C_{60}	10^8 M^{-1} s^{-1}	(14)
$R(M)_nC_{60}$• + R• → $R(M)_nC_{60}R$	10^8 M^{-1} s^{-1}	(15)
$R(M)_nC_{60}$• + $R(M)_n$• → $[R(M)_n]_2C_{60}$	10^8 M^{-1} s^{-1}	(16)
2 RC_{60}• ⇌ RC_{60}-$C_{60}R$	10^8 M^{-1} s^{-1} / 10^{-6} s^{-1}	(17)
$R(M)_nC_{60}$• + RC_{60}• ⇌ $R(M)_nC_{60}$-$C_{60}R$	10^8 M^{-1} s^{-1} / 10^{-6} s^{-1}	(18)
2 $R(M)_nC_{60}$• ⇌ $R(M)_nC_{60}$-$C_{60}(M)_nR$	10^8 M^{-1} s^{-1} / 10^{-6} s^{-1}	(19)
R• + $(C_{60})_x$ → $R(C_{60})_x$•	10^9 M^{-1} s^{-1}	(20)
$R(M)_n$• + $(C_{60})_x$ → $R(M)_n(C_{60})_x$•	10^9 M^{-1} s^{-1}	(21)
RC_{60}• + C_{60} ⇌ $R(C_{60})_2$•		(22)
$R(C_{60})_x$• + C_{60} ⇌ $R(C_{60})_{x+1}$•		(23)
$R(M)_n(C_{60})_x$• + C_{60} ⇌ $R(M)_n(C_{60})_{x+1}$•		(24)
RC_{60}• + M → $RC_{60}M$•		(25)
$R(M)_n$• + $R_x[R(M)_n]_yC_{60}$ → $R_x[R(M)_n]_{y+1}C_{60}$•		(26)
$R(M)_n$• + $[R(M)_n]_xC_{60}$-$C_{60}[R(M)_n]_y$ → $[R(M)_n]_{x+1}\dot{C}_{60}$-$C_{60}[R(M)_n]_y$		(27)

Figure 10. Mechanism of AIBN-initiated copolymerization of vinyl monomers with C_{60}.

propyl)-l,*x*-dihydro[60]fullerenes can be isolated from reaction mixtures in a combined yield of 18%.[27]

(5) NMR analyses of polymers formed by initiation with AIBN-α-^{13}C show that in both polystyrene/C_{60} and PMMA/C_{60} at low conversion 62−72% of the 2-cyano-2-propyl groups are bound to polymer chain ends, and 28−38% are bound to fullerenes.

(6) Neither the low molar mass AIBN/C_{60} adducts nor the polymers at any degree of conversion initiate further polymerization of monomer. Thus, the formation of 2-cyano-2-propyl to fullerene and polymer to fullerene carbon−carbon bonds is irreversible.

(7) After high conversion both polystyrene/C_{60} and PMMA/C_{60} contain much linear polymer.[20] The average number of fullerene units per molecule decreases with increasing reaction time. All polystyrene/C_{60} samples and some PMMA/C_{60} samples still contain an average of more than one fullerene unit per macromolecule at the high end of the molecular weight distribution.

(8) After high conversion, polymers from a 5:1 molar ratio of AIBN/C_{60} contain 6−7 atoms of nitrogen (which means 6−7 alkyl groups) per C_{60} unit.[20]

(9) Fullerene radicals remain in all of the solid polymers recovered at low and high conversion.

A radical mechanism to account for the results is shown in Figure 10. Estimated rate constants are given for many steps. Even Figure 10 simplifies a more complex problem, for it does not include most structures having more than two alkyl to fullerene carbon−carbon bonds, which are abundant as highly branched polymers at both low and high conversion. Equations 26 and 27 suggest addition steps that may begin the formation of polyalkyl fullerenes. We discuss the mechanism only in terms of dialkylfullerenes, but the discussion must also apply eqs 26 and 27 and succeeding steps (not shown) analogous to eqs 12−15 that produce polyalkylfullerenes.

Equations 8−11 are the conventional dissociation, initiation, propagation, and termination steps of radical chain polymerization that produce linear polystyrene or PMMA. The rate constants are extrapolations to 75 °C from literature data.[26,36−40] Equations 12 and 13 are the additions of initiator and polymer radicals to C_{60}. Rate

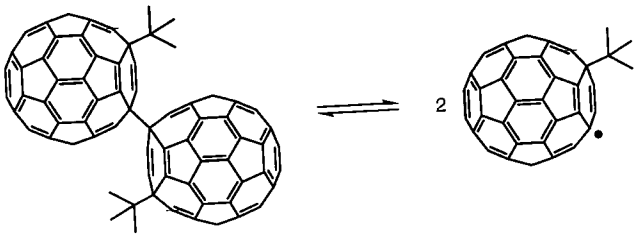


Figure 11. Dissociation of (*tert*-butyl-C_{60})$_2$.

constants for addition of most alkyl radicals to C_{60} at ambient temperature are $\geq 10^8$ M^{-1} s^{-1}.[41−44] The 2-cyano-2-propyl radical adds to C_{60} in 2-cyanopropane solution with a rate constant of 1.8×10^9 M^{-1} s^{-1}, and to a variety of C_{60} derivatives, including some of the polymers reported here, with rate constants of $\geq 1 \times 10^8$ M^{-1} s^{-1}.[45] Equations 14−16 are the terminations of initiator and polymer alkyl radicals by combination with alkyl-C_{60} radicals. We estimate that the rate constants for such processes are about 10^8 M^{-1} s^{-1} when at least one of the two combining radicals is small, and somewhat less when both radicals are long polymer chains, as in eq 11. Equations 12−16 explain the formation of dialkyl-C_{60} molecules, and further reactions of the dialkyl-C_{60} species, starting with eq 26, would produce tetra-, hexa-, and maybe octaalkyl-C_{60} molecules that could account for the branched polymers found by multidetector SEC. However, eqs 12−16 do not account for more than one fullerene unit per macromolecule.

Equations 17−19 are terminations by combination of fullerene radicals. The formation of fullerene−fullerene bonds is known from ESR investigations to be reversible.[46,47] Fullerene radicals were detected by ESR in all types of our polymer samples too. Reversible dissociation of (*tert*-butyl-C_{60})$_2$ is shown in Figure 11. We estimate from literature data[46] that the equilibrium constant at 75 °C for the dissociation of (*tert*-butyl-C_{60})$_2$ is 2×10^{-14} M. An estimated rate constant of 10^8 M^{-1} s^{-1} for combination of two small C_{60} radicals then gives a rate constant for dissociation of the fullerene−fullerene bond of 2×10^{-6} s^{-1}. Since (*tert*-butyl-C_{60})$_2$ has a much larger dissociation constant than (isopropyl-C_{60})$_2$,[46] (alkyl-C_{60})$_2$ compounds that are more hindered than (*tert*-butyl-C_{60})$_2$, such as our polymers, should have even larger dissociation constants and larger rate constants for the dissociation step. More 2-cyano-2-propyl and polymer radicals add to the compounds having fullerene−fullerene bonds, as in eq 27, to produce tetra-, hexa-, and octasubstituted difullerenes, which have branched structures that could account for the lower intrinsic viscosities of the polystyrene/C_{60} and the PMMA/C_{60} compared with linear polymers of equivalent hydrodynamic size. Dissociation of fullerene−fullerene bonds (eqs 17−19) followed by combination of the fullerene radicals with alkyl radicals (eqs 14−16) could also account for a decrease in the average number of C_{60} units per macromolecule from 30 to 120 min of reaction of MMA. Formation of homo-PMMA also reduces the average number of C_{60} units per macromolecule.

Still more microscopic reaction steps are needed to explain why any polymer chains at all are formed at low conversion. The initial concentrations in the oDCB solutions before AIBN decomposition were 3.3 M monomer and 4.6×10^{-3} M C_{60}. From these concentrations and the rate constants of eqs 9 and 12, the ratio of rates of addition of a 2-cyano-2-propyl radical to C_{60} and to monomer should be >100 (eq 28), and yet the NMR

$$\frac{k(\text{eq } 12)[C_{60}]}{k(\text{eq } 9)[\text{monomer}]} = \frac{(10^9\ M^{-1}\ s^{-1})(4.6 \times 10^{-3}\ M)}{(10^4\ M^{-1}\ s^{-1})(3.3\ M)} = 140 \quad (28)$$

spectra of Figure 9 prove that more 2-cyano-2-propyl radicals add to monomer than to C_{60}. This apparent contradiction is resolved if the C_{60} exists as clusters in the reaction mixtures rather than as monomeric C_{60}. The rate constant of addition of a radical per fullerene double bond in a cluster must be reduced by a factor of 100 or more compared with that of addition per double bond of monomeric C_{60}.

What are the structures of the clusters? There are several reports based on light scattering and other measurements that the sizes of C_{60} species in solution increase over time.[11,48−51] The fullerenes were assumed not to be covalently bonded. oDCB is one of the best solvents known for C_{60}. Three independent reports of the solubility are 22.9, 24.6, and 27.0 mg mL^{-1} at 25 °C,[9,10,52] but the solubility reaches a maximum at 37 °C and declines to about 15 mg mL^{-1} at 75 °C.[52] Our polymerizations were carried out with 7.5 mg of C_{60}/mL of 2:1 v/v oDCB/monomer at 75 °C. The solubilities of C_{60} in the monomers and in the oDCB/monomer mixtures are not known. One possible type of cluster that could account for the slow relative rates of addition of radicals to C_{60} is noncovalent aggregates, represented as $(C_{60})_x$ in eqs 20 and 21. Such clusters could be either soluble or insoluble in the oDCB/monomer mixtures. If they are insoluble, they must redissolve as the reaction proceeds, because the product mixtures are soluble. Most C_{60} derivatives, including our polymers, are more soluble than C_{60} itself.

A second possible type of cluster is poly-C_{60} with covalent fullerene−fullerene bonds.[19] Although AIBN initiates polymerization of C_{60} in oDCB at 75 °C in the absence of monomer, as shown in Figure 7, there was still monomeric C_{60} in the reaction mixtures detected by SEC at room temperature after 10-fold dilution into toluene. That amount of monomeric C_{60} must not have been present in the polymerizing mixture, because 2-cyano-2-propyl radicals add to free C_{60} much faster than to monomer. If the clusters are covalently linked fullerene polymers formed via eqs 22 and 23, (a) they must form much faster than radicals add to monomers, (b) the rate constant of addition of a radical to a double bond in a cluster must be <0.01 times the rate constant of addition to a double bond in monomeric C_{60} to allow 2-cyano-2-propyl radicals to add to monomer faster than to fullerene polymers, and (c) many fullerene−fullerene bonds must dissociate during isolation and storage of the samples (for weeks) before SEC analysis. These restrictions are required to account for PMMA/C_{60} and polystyrene/C_{60} formation. Consequently covalent structures seem less likely than noncovalent structures for the C_{60} clusters.

We have neither proved nor disproved propagation by addition of C_{60} radicals to monomers (eq 25), which could account for the formation of polymers with many fullerene units. However, if it exists at all, eq 25 must be irreversible, because in control experiments neither di(2-cyano-2-propyl)- nor polymer-substituted fullerenes initiated polymerization of monomers.

There are several possible explanations for why polystyrene/C_{60} contains much larger numbers of fullerene units per macromolecule than PMMA/C_{60} at the high end of the molecular weight distribution and why polystyrene/C_{60} incorporates much less monomer during the first 120 min of reaction. Perhaps C_{60} radicals propagate by addition to styrene more readily than to MMA, so that C_{60} forms true copolymers with styrene but not with MMA. A second possibility is that the C_{60} clusters are smaller in the styrene reaction mixture than in the MMA reaction mixture, and because of a higher concentration of the smaller C_{60} clusters, the C_{60} reacts faster in styrene. A third possibility is that a fullerene radical substituted with a secondary alkyl polystyryl chain propagates by addition to another fullerene faster than does a fullerene radical substituted with a tertiary alkyl PMMA chain. The reasons for the differences between the polystyrene/C_{60} and the PMMA/C_{60}, and the nature of the C_{60} clusters in the reaction mixtures, are subjects for further investigation.

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