Incorporation of C_{60} into Poly(methyl methacrylate) and Polystyrene by Radical Chain Polymerization Produces Branched Structures

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ABSTRACT: Polymerizations of styrene and methyl methacrylate (MMA) containing 1 wt % C_{60} initiated by 5 or 10 mol of azobis(isobutyronitrile)/mol of C_{60} in 1,2-dichlorobenzene solution produce brown polymers in 53−97% yield with all of the C_{60} incorporated, linear polymer equivalent molecular weights of P_n = 19 000−31 000, and $P_w/P_n < 2$. There are short induction periods before polymerization begins. All of the C_{60} is incorporated into the polymer after low conversion of the monomer. Multidetector size exclusion chromatography analyses measured polymer mass by differential refractive index, M_w by two-angle laser light scattering, intrinsic viscosity by differential viscometry, and mass of only C_{60} derivatives by UV. Molar chromatograms show that all of the polymer at the high end of the molecular weight distributions contains C_{60}, and there are sizeable amounts of a lower molecular weight linear polymer. The high molecular weight polystyrene contains as many as 10−100 C_{60} units, but the high molecular weight PMMA contains an average of one C_{60} unit per macromolecule. All of the polymers have lower intrinsic viscosities and higher M_w than linear standards of the same retention volume due to branched or star structures. Calculations from a random branching model of Zimm and Stockmayer indicate that the PMMAs have an average branch number of five over the entire molecular weight distribution and systematically increasing average branch lengths with an increasing degree of conversion.

Introduction

Since the first production of gram amounts of C_{60},[1] many types of polymers containing C_{60} on a side chain or in the main chain have been reported, but few have been characterized well and little is known about their properties.[2−4] Among the most difficult to analyze are those produced by radical chain reactions. The first such polymer, prepared by radical polymerization of C_{60} and *p*-xylylene,[5] was totally insoluble and was identified by solid state NMR spectra. Subsequently soluble polystyrene and poly(methyl methacrylate) (PMMA) containing C_{60} were prepared in bulk and in solution by thermal initiation.[6−13] As much as 50 wt % of C_{60} has been incorporated into polystyrene by radical chain reactions, and weight-average molecular weights as high as 20 000 have been found for polystyrene containing 30 wt % C_{60}.[11] All of these polymers are brown, the color of mixtures of derivatives of C_{60}, and some of them can be cast as films of quality suitable for spectrophotometry.

It is surprising that polymers are even produced in the presence of C_{60}, because rate constants of 10^8−10^9 M^{-1} s^{-1} for the addition of benzyl, methyl, *tert*-butyl, and other radicals to C_{60} have been measured in solution by pulse radiolytic and electron spin resonance (ESR) spectroscopic methods.[14−17] These are 10^5 times greater than the rate constants for propagation of polystyryl and PMMA radicals,[18] greater than the rate constants of bimolecular termination of polymerization of styrene and MMA,[18] and of the same order of magnitude as the rate constants for the combination of nitroxyl radicals with polystyryl radicals.[19] Moreover, not one but many alkyl radicals can add to a single C_{60} molecule. The structural units identified by esr spectroscopy include allyl radicals and cyclopentadienyl radicals formed by the addition of three and five radicals radially around a five-membered ring of C_{60}, and mass spectra of the products of the addition of alkyl radicals to C_{60} have revealed up to 15 benzyl groups and 30 methyl groups bound to C_{60}.[20,21]

In this paper we report analyses of the compositions and molecular weight distributions of polystyrene and PMMA containing C_{60} by multidetector size exclusion chromatography (SEC) and suggest possible mechanisms to explain the paradox of how C_{60} can be incorporated into high molecular weight polymers by radical chain polymerization.

Experimental Section

Materials. C_{60} (Mer Corp., Tucson, AZ) was 99.5% pure. Monomers from Aldrich Chemical Co. or Polysciences Inc. were distilled under vacuum before use.

Polymerizations. In a typical polymerization 25 mg of C_{60} in 4.0 mL of 1,2-dichlorobenzene (*o*-DCB) and 28 mg (5 mol/mol of C_{60}) of azobis(isobutyronitrile) (AIBN) in 1.0 mL of oDCB were sonicated separately for 1 h. The oDCB solutions and 2.5 g of styrene or MMA were combined in a 15 mL test tube and sparged with nitrogen for 5 min. The tube was sealed with a rubber septum and placed in an oil bath at 75 °C. Samples were withdrawn periodically by syringe, precipitated into hexanes, redissolved in THF, and reprecipitated into hexanes. Samples were collected by filtration through fritted filters, or if solid particles were too fine by centrifugation for 1−2 h using a benchtop centrifuge. All samples were dried under vacuum at 25 °C.

SEC. The SEC system at Kodak consisting of ultraviolet absorption (UV), two-angle light scattering (TALLS), differential viscometry (DV), and differential refractive index (DRI) detectors in serial configuration is similar to a multidetector SEC system described in detail previously.[22] Typical chromatograms of a PMMA/C_{60} are shown in Figure 1. The

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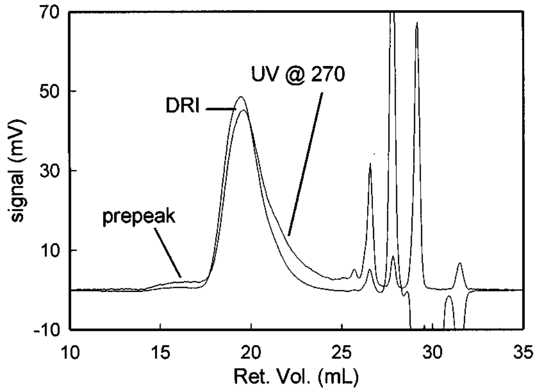


Figure 1. Chromatograms of PMMA/C_{60} sample 87016. Note the low retention volume prepeak at 14−17.5 mL.

prepeak in these chromatograms is apparently an artifact, probably caused by a small amount of aggregated C_{60} rich material. We determined this from three pieces of evidence: (1) It absorbs strongly in the UV, but gives a weak DRI response, indicating it contains a high percentage of C_{60}. The UV response of the prepeak is 3.06% of the total peak area, and the DRI prepeak is 0.38% of the total peak area, or ~0.38% of the total sample mass in the worst case (sample 87016). (2) It has little viscosity, indicating that it has a compact structure. (3) It gives an odd optical effect, leading to no right angle light scattering and a decrease in the base line of the low-angle light scattering detector. This is inconsistent with a high polymer. The prepeak probably is an aggregate of small moleules rich in C_{60}. Since it is less than 0.4% of the total mass, it has been excluded from molecular weight analyses, calculations of C_{60} contents, and branching calculations. There were no such prepeaks in the chromatograms of polystyrene/C_{60} samples.

Results

We showed earlier that both styrene and MMA could be polymerized in the presence of 1−10% by weight C_{60} by thermal initiation with 5 mol of AIBN/mol of C_{60} in oDCB solution.[8] C_{60} is much more soluble in oDCB than in either monomer, or in benzene or toluene, the solvents used by other investigators of polystyrene/C_{60}. Our isolated yields of PMMA and of polystyrene after 16 h at 75 °C were about 90% and 70%, respectively, in many experiments. Elemental analyses of products from 5 mol of AIBN/mol of C_{60} in the absence of a monomer showed about six nitrogen atoms, due to 2-cyano-2-propyl groups, per C_{60} unit.

Polymer Yield and Molecular Weight Dependence on Time. Figure 2 shows yields of isolated polymers as a function of reaction time at 75 °C for PMMA/C_{60} and polystyrene/C_{60}. Yields of polymers are low at reaction times of 2 h, and there is no acceleration of polymerization at intermediate reaction times. From dilatometric kinetic measurements Cao and Webber[10] found an induction period prior to polymerization of styrene and C_{60}, whereas Stewart and Imrie[24] found no induction period. Although our measurements of monomer conversion by isolation of the polymer are crude compared with the kinetic measurements, they support the polystyrene results of Cao and Webber. Figure 3 shows that the polystyrene equivalent molecular weights of the PMMA samples increase to approximately constant values at ≥10 h, and the molecular weights of the polystyrene samples reach an approximately constant value after 6 h.

C_{60} Contents of Polymers As a Function of Molecular Weight. The DRI detector measures the weight concentration of the sample at each point of the chromatogram, c_i, provided the specific refractive index increment of the polymer remains constant across the distribution. We believe this to be true, even for a polymer that has inhomogenoeously incorporated C_{60} across the molecular weight distribution because of the low concentrations of C_{60} involved. The DRI response

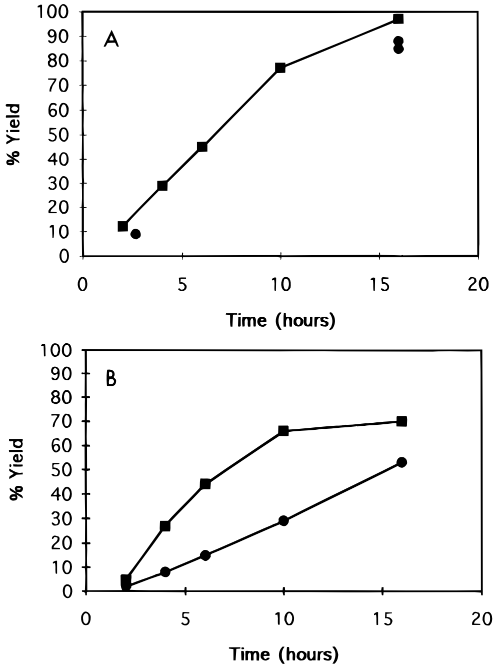


Figure 2. Yields of insoluble products vs time for polymerization of (A) MMA with 1 wt % C_{60} with a 5/1 AIBN/C_{60} molar ratio at 75 °C. Samples from a single experiment are connected by lines. The other data points are from independent experiments. (B) Two polystyrene data sets from (a, circles) 5/1 AIBN/C_{60} molar ratio (samples 89xxx in Table 1), and (b, squares) 10/1 AIBN/C_{60} molar ratio (samples 98xxx in Table 1) under otherwise the same conditions.

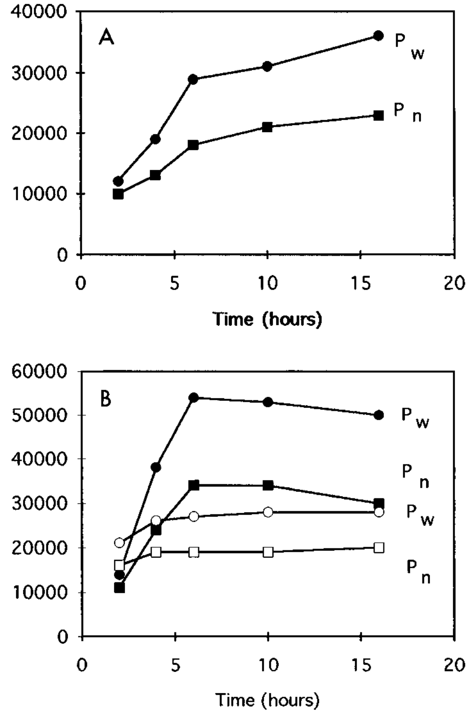


Figure 3. (A) Polystyrene equivalent molecular weights from UV detection at 220 nm vs time of polymerization of MMA with 1 wt % C_{60} using 5/1 AIBN/C_{60}. (B) Polystyrene/C_{60} using 5/1 AIBN/C_{60} (closed symbols) and 10/1 AIBN/C_{60} (open symbols).

is used to construct the molar chromatogram by dividing each concentration by its molecular weight,[25]

$$[c_i] = \frac{c_i}{M_i} \tag{1}$$

where M_i is the absolute molecular weight measured either from the light-scattering detector or from the viscometry detector through a universal calibration curve. The quantity $[c_i]$ is the molar concentration of polymer molecules at point i, and the total moles of the polymer is the integral of the molar chromatogram. The UV chromatogram obtained at a wavelength selective only for C_{60} is proportional to the molar concentration of C_{60} at each data point, $[c_{60,i}]$ through the height, $F_{N,i}$, of the normalized UV chromatogram,

$$[c_{60,i}] = \frac{F_{N,i} m_t}{\Delta v_i} \tag{2}$$

where m_t is the total moles of C_{60} injected and Δv_i is the volume increment between data points. The integral of the C_{60} molar chromatogram is the total moles of C_{60} or m_t. The area of the $[c_{60,i}]$ molar chromatogram is compared to the area of the polymer molar chromatogram to estimate the average incorporation of C_{60} on a molar basis. The number of C_{60} units at each retention volume, p_i, is

$$p_i = \frac{F_{N,i} m_t}{\left[\frac{c_i}{M_i}\right] \Delta v_i} \tag{3}$$

where $[c_i/M_i]$ is from the DRI chromatogram. The total moles of C_{60}, m_t, is assumed to be that for 1 wt % C_{60} in the 97% yield of PMMA/C_{60} sample, 87016 (Table 1). This sample is also used to calculate the molar response factor of C_{60} at 270 nm from the area under the UV chromatogram and is used to calculate the molar concentration of C_{60} in the PMMA samples of lower conversion. The calculations assume that the molar absorptivity of C_{60} units at 270 nm is constant throughout the series of samples.

Molar chromatograms of the highest and lowest conversion PMMA samples are shown in Figure 4. The area of each molar chromatogram obtained from the UV response is lower than that of the polymer molar chromatogram, indicating that some fraction of polymer chains does not contain C_{60}. The ratio of areas of UV and polymer molar chromatograms (Table 1) is the number average of C_{60} molecules per polymer chain for the entire distribution. If it is assumed that a maximum of one C_{60} molecule is incorporated per polymer molecule, then the moles of polymer not containing C_{60} is the difference in molar chromatogram areas. This provides a minimum estimate for the amount of linear PMMA of 32 mol % for the lowest conversion sample to 62 mol % at the highest conversion. The number of C_{60} units per polymer molecule, p_i, decreases from a maximum value near 1.0 with increasing retention volume (decreasing molecular weight), consistent with the dilution of PMMA/C_{60} molecules with low molecular weight linear PMMA that does not contain C_{60}.

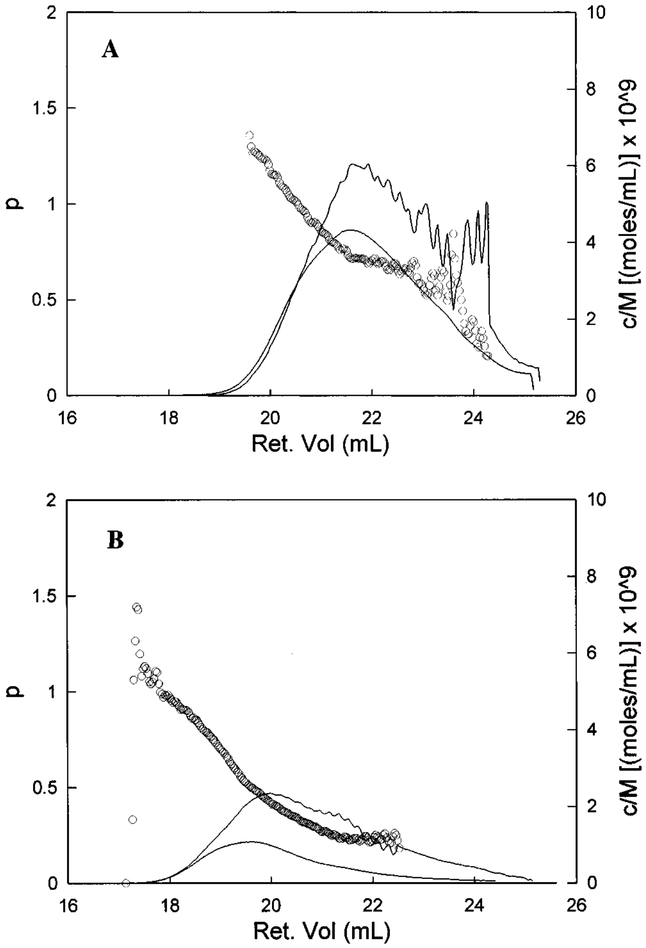


Figure 4. Molar chromatograms of PMMA/C_{60} samples (A) 87002 and (B) 87016. Upper curve, mass detection; lower curve, C_{60} detection; p = fraction of molecules containing C_{60} derivatives, circles.

Polystyrene/C_{60} present a somewhat different picture. The UV chromatogram at 270 nm is now not selective for C_{60} because of the absorbance of polystyrene at this wavelength. Fortunately, polystyrene absorbs 270 nm radiation much less strongly than C_{60}, and its contribution to the UV chromatogram is subtracted as the normalized DRI concentration chromatogram multiplied by the molar UV response factor for polystyrene at 270 nm. The average incorporation of C_{60} in the 89xxx (xxx = hours reaction time) series (Figure 5), prepared with 5 mol of AIBN/mol of C_{60}, is always greater than 1.0 C_{60} units/molecule after 6 h of reaction time and less than 1.0 for the lower molecular weight components after 16 h, which is consistent with polymer molecules that do not contain C_{60}. Again, the average number of C_{60} molecules per polymer molecule decreases with increasing conversion. However, the average incorporation is much less for series 98xxx (not shown), which were prepared with 10 mol of AIBN/mol of C_{60}. The number of C_{60} molecules per polymer molecule increases sharply with decreasing retention volume (Figure 5), indicating that high molecular weight polymer molecules contain multiple C_{60} units. Sun and co-workers also reported many C_{60} units per macromolecule in samples containing 1.7−50% C_{60} by weight.[11] They also found that the molar absorptivity per C_{60} unit at 350 nm was constant through the range of compositions of the samples, which supports the assumption used to calculate the molar chromatograms.

Visual observations also indicate that most of the C_{60} is incorporated early in the polymerizations. During isolations of the 87xxx series of PMMA/C_{60} samples, the hexane filtrates from first precipitation of the polymer were colored pale apricot from 87002, pale yellow from 87004, and colorless from 87006. Since the color of C_{60}

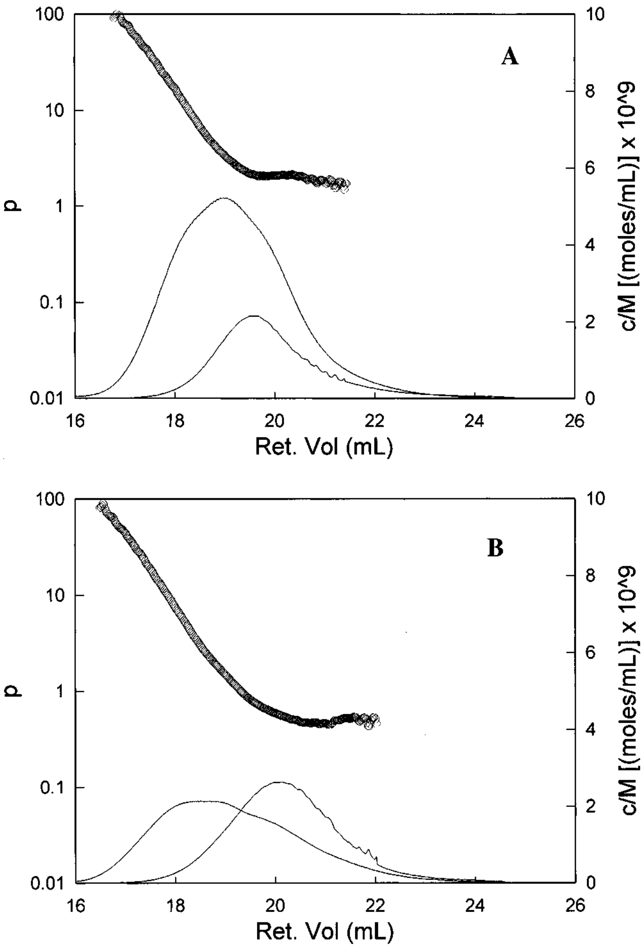


Figure 5. Molar chromatograms of polystyrene/C_{60} samples: (A) 89006 and (B) 89016. Curve starting at low retention volume, C_{60} detection; curve starting at longer retention volume, mass detection; p = fraction of molecules containing C_{60} derivatives, circles.

solution in hexane is magenta, there is no significant amount of C_{60} in the MMA reaction mixture even after 2 h. The apricot and yellow colors indicate low concentrations of soluble C_{60} derivatives. The hexane filtrates from the polystyrene/C_{60} samples 89xxx and 90xxx had the colors of strong tea, weak tea, and very dilute tea after 2, 4, and 6 h, respectively. 1,2- and 1,4-disubstituted C_{60} compounds[26,27] and mixtures of substituted C_{60} compounds are brown. None of the filtrates from the isolation of samples at low conversion were intensely colored enough to account for a major fraction of the C_{60}.

Multidetector SEC. The weight-average molecular weight of the whole polymer is calculated from the mass injected and the integrated two-angle light-scattering (TALLS) detector response.[28] The whole polymer intrinsic viscosity is obtained from the mass injected and the integrated differential viscometry (DV) detector reponse.[29] In both cases, a concentration detector is not required. The DRI concentration response is combined with a molecular-weight-sensitive detector response at each point of a chromatogram to calculate “local” properties, defined as the concentration, viscosity, and molecular weight at each point of the chromatogram. TALLS combined with DRI provides the local weight-average molecular weight, and DV combined with DRI calculates the local intrinsic viscosity.

Samples containing C_{60} have lower local intrinsic viscosities and higher local molecular weights (Figure 6) than those of linear polystyrene of equivalent hydrodynamic volume (equivalent retention volume). This is the expected result for stars and branched polymers. The differences between local viscosities and molecular weights of polystyrene/C_{60} and linear polystyrene are most pronounced at large sizes (early retention volumes) and deviate most for the low-conversion sample, approaching the linear model with increasing conversion. Absolute molecular weight averages and whole polymer intrinsic viscosities for members of the three series are provided in Table 1. Molecular weights are higher than those for linear chain equivalents, which is consistent with some level of branching in all samples. Comparison of local values of branched polymers to values for chemically similar linear polymers at equivalent molecular weight is used to estimate branching in samples.

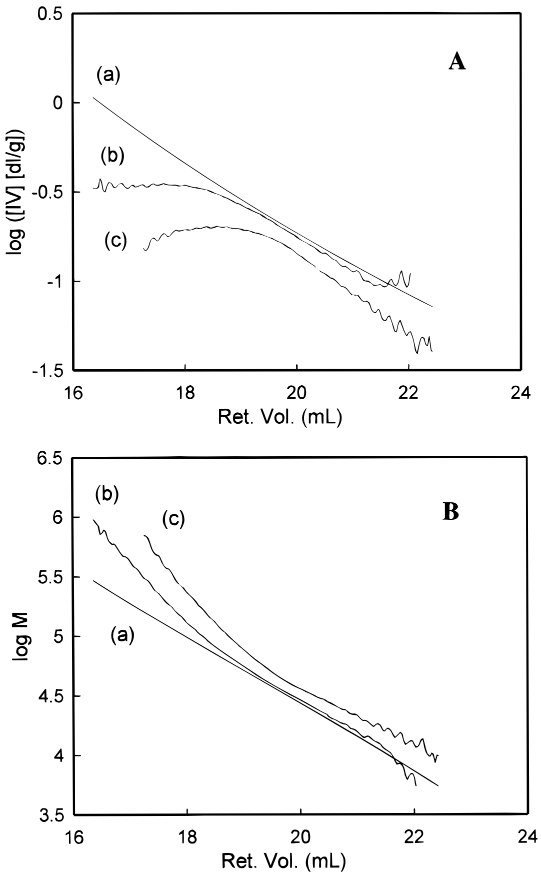


Figure 6. (A) Intrinsic viscosities and (B) absolute molecular weights as a function of retention volume of (a) linear polystyrene compared with polystyrene/C_{60} samples, (b) 89004, and (c) 89016.

The molar chromatograms of PMMA/C_{60} showing an average of no more than one fullerene unit per macromolecule in the high end of the molecular weight distribution, even at low conversion to polymer, suggest a star model for the structure with branches of random length extending from a fullerene core. In contrast, the molar chromatograms of polystyrene/C_{60} showing 10–100 fullerene units/macromolecule in the high end of the molecular weight distribution suggest a more complicated branched structure. As an example of how the SEC results can be used to calculate numbers and molecular weights of branches, we have applied a random star model to emphasize further the differences between the structures of the PMMA/C_{60} and the polystyrene/C_{60}. The star model would be appropriate for the polystyrene/C_{60} structures only if they consist of clusters of C_{60} with many polymer branches. That is

Table 1. Analyses of Polymers Isolated after Varied Conversion Times

lab no.	sample	% yield	M_n	M_w	$[\eta]$ dL/g	P_n[b]	P_w[c]	$[c_{60}]/[c_i]$	limiting arm M_n
87002	PMMA/C_{60}	12	10 070	18 100	0.088	9360	15 600	0.68	
87004	PMMA/C_{60}	29	19 550	30 950	0.118	15 900	26 100	0.60	
87006	PMMA/C_{60}	45	21 600	43 250	0.172	23 800	39 400	0.44	
87010	PMMA/C_{60}	77	29 550	51 850	0.174	26 800	44 700	0.45	
87016	PMMA/C_{60}	97	33 800	54 900	0.163	26 400	44 800	0.38	
89004	PS/C_{60}	8	34 850	65 600	0.147	23 600	38 000	*a*	6700
89006	PS/C_{60}	15	43 300	74 050	0.218	35 300	52 300	3.21	11 900
89010	PS/C_{60}	29	40 650	69 750	0.239	36 500	53 200	1.65	14 700
89016	PS/C_{60}	53	33 100	65 800	0.228	30 800	49 700	1.13	13 900
90006	PS/C_{60}	21	39 350	61 950	0.220	32 300	48 100	2.25	12 800
90010	PS/C_{60}	35	37 300	65 350	0.251	34 800	53 300	2.19	17 900
90016	PS/C_{60}	55	36 750	68 000	0.262	34 400	56 700	0.90	22 700
98004	PS/C_{60}	27	19 950	32 700	0.157	17 900	26 900	0.86	8900
98006	PS/C_{60}	44	19 750	32 350	0.165	18 700	27 700	0.57	10 000
98010	PS/C_{60}	66	19 300	32 600	0.172	18 400	28 700	0.41	11 900
98016	PS/C_{60}	70	21 150	35 650	0.178	19 500	31 000	0.37	19 400

[a] Not determined. [b] P_n = linear equivalent number-average molecular weight. [c] P_w = linear equivalent weight-average molecular weight.

only one of several possibilities, which are in the Discussion. Although the model may not be appropriate for the polystyrene/C_{60}, related models for branched polymers would show the same qualitative but somewhat different quantitative results.

In the random star model the relationship between number of arms, f, and the ratio of root-mean-square radii of branched and linear polymers, g, has been established for the unperturbed state on the basis of equations given by Zimm and Stockmayer[30-32] using random flight statistics:

$$g = \frac{6f}{(f+1)(f+2)} \tag{4}$$

The parameter g is not directly available because we are unable to accurately measure isotropic scatterers with root-mean-square radii of less than ≈12 nm by TALLS on these samples. Instead, we measure the effect of branching on the intrinsic viscosity expressed by the parameter g', the ratio of branched polymer intrinsic viscosity to linear polymer intrinsic viscosity at equivalent molar mass,

$$g' = \frac{[\eta]_{b,M}}{[\eta]_{i,M}} \tag{5}$$

and estimate g from

$$g' = g^{\epsilon}$$

The empirical structure factor ϵ depends on the type of branching and contains excluded volume and other effects. Recent results on asymmetric six arm stars in tetrahydrofuran[25] provide an estimate $\epsilon \sim 0.8$. The number of arms estimated from eqs 3–5 as a function of molecular weight is shown for series 90xxx in Figure 7A. The data are not meaningful at low molecular weights because of the presence of significant amounts of linear polymer not containing C_{60}. In the high molecular weight region where little linear polymer is present, the number of arms increases with increasing molecular weight. The number-average molecular weight of arms, estimated by dividing the molecular weight by the number of arms, is plotted in Figure 7B. Arm molecular weights are approximately constant above log M = 5 and increase with increasing conversion. The molecular weights of arms for each series member in this constant region are given in Table 1.

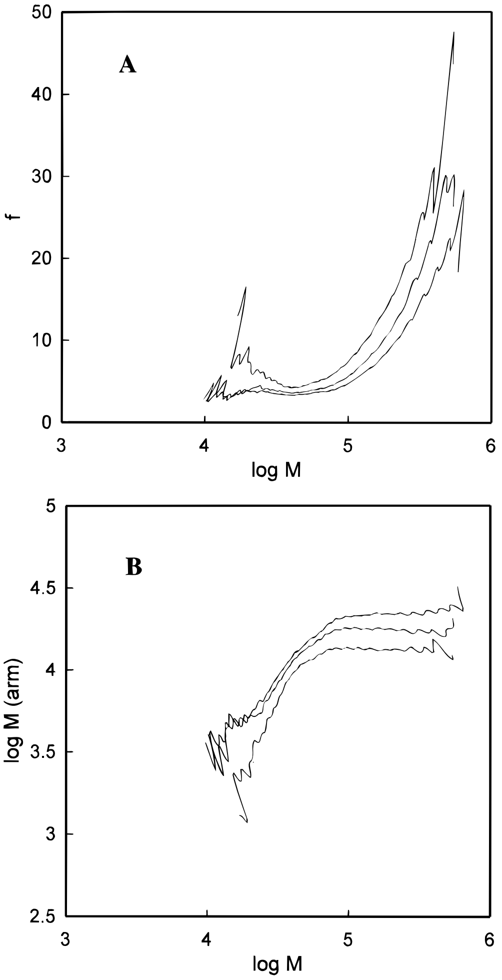


Figure 7. (A) Branch number f as a function of molecular weight and (B) M_n of arms of polystyrene/C_{60} samples 90006, 90010, and 90016. Curves in each graph are within experimental error of one another.

Divergence of the log $[\eta]$ − retention volume plots for PMMA/C_{60} from linear PMMA samples is not observed. Instead, all plots are displaced to lower viscosities but parallel to that of linear PMMA (Figure 8A). Molecular weights are higher than linear PMMA at equivalent hydrodynamic volumes (Figure 8B), again consistent with branched structures. The average number of arms is approximately 5–6 for all PMMA samples and shows no appreciable change as a function of molecular weight

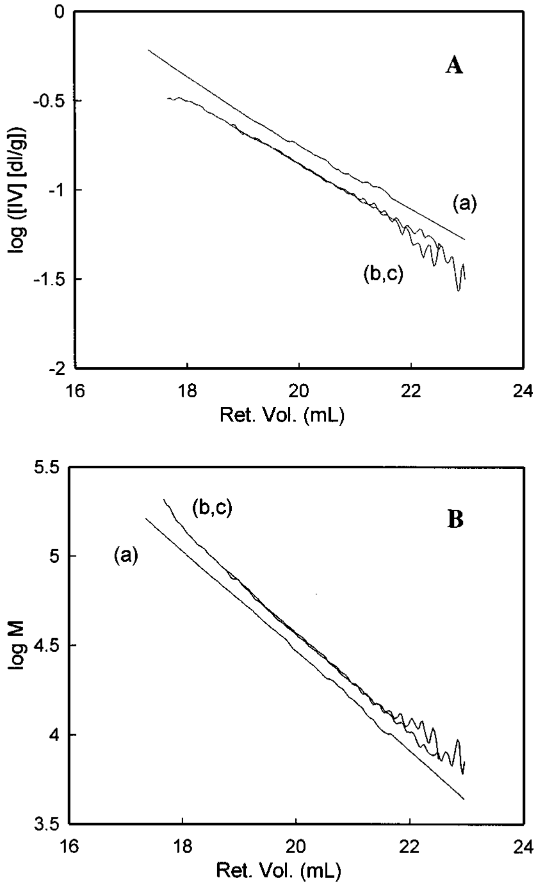


Figure 8. (A) Intrinsic viscosities and (B) absolute molecular weights as a function of retention volume of (a) linear PMMA compared with PMMA/C_{60} samples, (b) 87004, and (c) 87016.

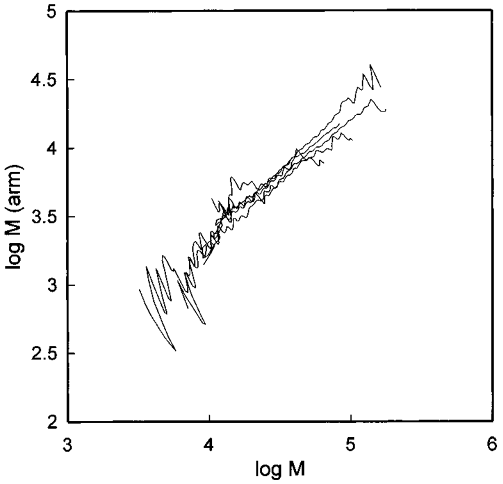
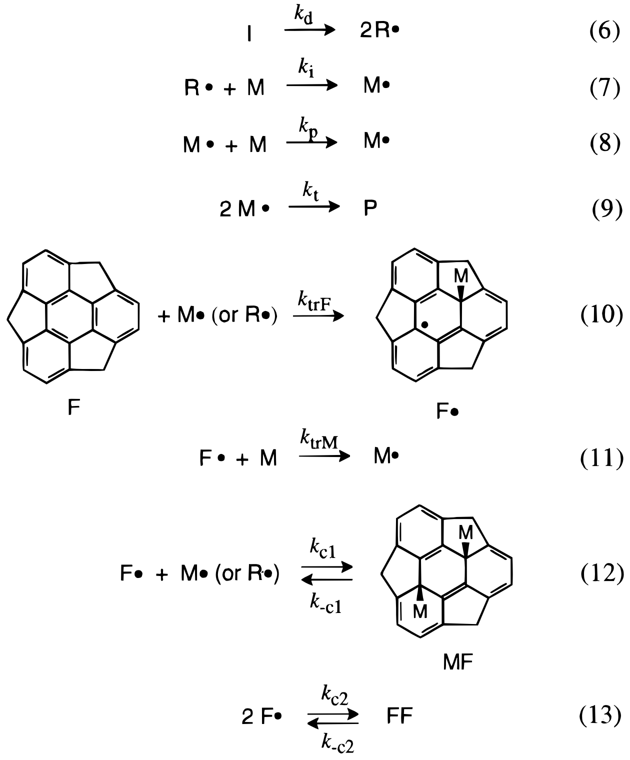


Figure 9. M_n of arms of all five PMMA/C_{60} samples in series 87xxx as a function of polymer molecular weight.

Scheme 1



in the range log $M = 4-5$. We know that the low molecular weight region contains appreciable amounts of linear polymer, and this decreases the estimate of the number of arms. This implies that the number of arms asymptotically decreases with increasing molecular weight of PMMA, reaching a constant value of 5−6 arms in the high molecular weight region. Correspondingly, the molecular weight of arms appears to increase with increasing molecular weight (Figure 9) and does not reach a limiting value as observed with polystyrene/C_{60}. One interpretation of these calculations is that the basic structure of the PMMA/C_{60} is established early and continued polymerization only increases the lengths of the arms. Another interpretation is that increasing amounts of linear polymer are produced with increasing conversion, and the number of arms of the star fraction of the sample also increases so that there is a constant average number of arms throughout the range of samples.

Discussion

Mechanisms for polymerization of styrene and of MMA in the presence of 1 wt % C_{60} must be consistent with the following observations.

(1) C_{60} reacts with alkyl radicals at rate constants of 10^8-10^9 L mol^{-1} s^{-1},[14−17] which are nearly diffusion controlled.

(2) There are short periods of inhibition before polymerization begins.

(3) The C_{60} is completely consumed when only 10% of MMA or styrene is converted to a polymer.

(4) All of the polymers have lower intrinsic viscosity and higher molecular weight than linear polystyrene and PMMA of the same retention volume in SEC experiments. The structures must be branched.

(5) The M_n and M_w of the PMMA samples increase throughout the polymerization. Simultaneously increasing amounts of lower molecular weight linear PMMA are formed.

(6) The polystyrene at all extents of conversion contains larger amounts of C_{60} units at the high molecular weight end of the distribution.

(7) The M_n and M_w of polystyrene samples isolated at varied times are about the same throughout the polymerization due to the simultaneous increase of the molecular weight of a C_{60}-containing polymer and production of a lower molecular weight linear polymer.

A general mechanism to describe the polymerization of both MMA and styrene with C_{60} and notation for the rate constants of microscopic steps is shown in Scheme 1. We neglect hydrogen atom chain transfer to the monomer, solvent, and initiator.

In Scheme 1, I = initiator, AIBN, which dissociates thermally into two radicals $R^\bullet$, with rate constant k_d. M = monomer, which adds $R^\bullet$ at rate constant k_i to produce monomer-ended radical $M^\bullet$. The $M^\bullet$ adds to M at propagation rate constant k_p, which is on the order of 10^3 L mol^{-1} s^{-1} at 75 °C,[18] and two $M^\bullet$ terminate by combination or disproportionation at rate constants k_t in the range $2-8 \times 10^7$ L mol^{-1} s^{-1}.[18] Radicals $R^\bullet$ from the initiator and chain radicals $M^\bullet$ add to fullerene F to form fullerene radicals $F^\bullet$ with the transfer rate constant k_{tr}. C_{60} is known to accept a first alkyl radical such as benzyl, methyl, or *tert*-butyl at a rate constant of $\geq 10^8$ L mol^{-1} s^{-1},[14-17] and to form polyalkylated C_{60}.[20,21] Stewart and Imrie detected C_{60} radicals in polymerizing solutions of styrene and C_{60}.[24]

We consider two possible routes to macromolecules containing many F units: (a) many combinations of fullerene radicals $F^\bullet$ (eq 13) and (b) copolymerization by addition of $F^\bullet$ to monomer M (eq 11) as well as addition of $M^\bullet$ to F (eq 10) or a combination of $M^\bullet$ with $F^\bullet$ (eq 12). The addition of $F^\bullet$ to M (eq 11) is expected to have a smaller rate constant than the propagation of $M^\bullet$, because $F^\bullet$ is more stable than $M^\bullet$ and $F^\bullet$ has a bulky 2-cyanopropyl group or a polymer chain located at 1,4 to the site where the monomer would likely add. Whether or not eq 11 contributes to polymer formation, numerous $R^\bullet$ and $M^\bullet$ must add to each F unit to form MF bonds (eq 10). If eq 11 does not contribute, no polystyrene or PMMA can form until F has enough alkyl substituents to reduce the rate constant k_{trF} for further addition of $M^\bullet$ and $R^\bullet$ to F to within an order of magnitude of the rate constant k_p for propagation of $M^\bullet$. F represents a distribution of fullerenes with different numbers of both R and M substituents.

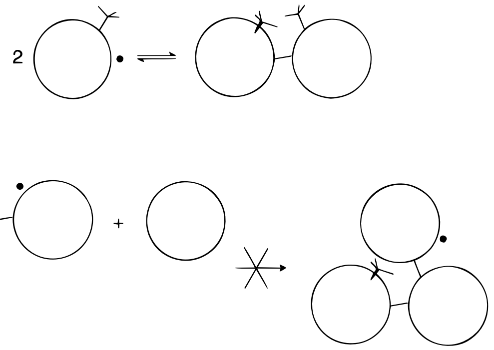
Radicals $M^\bullet$ and $R^\bullet$ combine with $MF^\bullet$ also to form MF (and RF) bonds at the rate constant for combination k_{c1}. If the formation of MF and RF bonds is reversible (eq 12), the fullerene might act as a "stable" free radical for controlled polymerization to produce branched polymers. Similarly, two fullerene radicals $F^\bullet$ combine (reversibly) to form FF bonds (eq 13).

As previously suggested by Cao and Webber,[10] we omit propagation of fullerene radicals (eq 14). Sun and

$$F^\bullet + F \rightarrow F^\bullet \tag{14}$$

co-workers suggested that both eqs 13 and 14 could account for the formation of polymers containing many fullerene units.[11] We suggest that eq 14 is insignificant because (1) Reactions in the literature that form two new bonds to C_{60} sequentially occur either at 1,2 or 1,4 in a six-membered ring, with 1,2-addition favored when the substituting groups are small and 1,4-addition favored when they are large (eq 12).[2] Two substituents on one six-membered ring minimize the energetically unfavorable formation of fullerene 5,6-double bonds.[2] (2) Molecular mechanics models of the 1,4-linked di-*tert*-butyl-C_{60} dimer (Scheme 2) show strong nonbonded repulsion between each *tert*-butyl group and the opposing C_{60} unit,[33] which causes the dimer to dissociate reversibly at ambient temperature. The equilibrium constants for dissociation have been calculated from ESR measurements over a wide range of temperature.[34] Note that dimerization of the *tert*-butyl-C_{60} radical is the same as the coupling step (eq 13) during polymerization if the *tert*-butyl group is replaced by an initiator group or a polymer chain. Since a C_{60} unit should have stronger repulsive nonbonded interactions than the smaller *tert*-butyl group, formation of a C_{60} unit bonded at 1,4 to two other C_{60} units (Scheme 2) is unlikely.

Scheme 2



The SEC molar chromatograms of the polystyrene/C_{60} samples prove the presence of species containing as many as 10−100 C_{60} units. In the mechanism of Scheme 1 this requires either that copolymerization (eq 11) leads to polymer chains connecting F units, or that eq 13 provides multi-F structures via coupling of fullerene radicals. The coupling mechanism would produce a star structure having a core of many fullerenes and many branches. The copolymerization would produce a similar star structure if the chain lengths between fullerenes are very short, or a structure in which fullerene units are beadlike kinks in chains of highly branched polymers if chain lengths between fullerenes are long. At this time we lack evidence to distinguish among these possible structures.

Conclusion

Radical polymerizations of styrene and MMA in the presence of C_{60} form branched structures. The C_{60} is incorporated into the polymer early. Using the power of multidetector SEC analyses, we have shown for the first time for copolymers of C_{60} with vinyl monomers (1) absolute M_w and M_n of the polymers, (2) numbers of fullerene units per macromolecule across the entire molecular weight distribution, (3) increasing amounts of a linear polymer formed with increasing reaction time, (4) lower molecular weight of the linear polymer molecules than that of the branched molecules containing C_{60}, (5) many fullerene units per macromolecule at the high end of the molecular weight distribution of polystyrene/C_{60} but only one fullerene unit per macromolecule of PMMA/C_{60} even at high molecular weight, and (6) estimates of the numbers of branches per macromolecule across the molecular weight distributions. The major unanswered questions about the mechanism are (1) Do fullerene radicals propagate by addition to the monomer? (2) Does fullerene act as a labile end group in a controlled radical polymerization? (3) What are the structures of the branched polystyrene/C_{60} materials? Experiments to address these questions are planned.

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References and Notes

(1) Kratschmer, W.; Lamb, L. D.; Fostiropaulus, K.; Huffman, D. *Nature* **1990**, *347*, 354.

(2) Hirsch, A. *The Chemistry of Fullerenes*; Georg Thieme Verlag: Stuttgart, 1994.
(3) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996; pp 320−325.
(4) Ford, W. T.; Lary, A. In *Polymer Data Handbook*; Mark, J. E., Ed.; Oxford University Press: New York, 1997; in press.
(5) Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977.
(6) Cao, T.; Webber, S. E. *Macromolecules* **1995**, *28*, 3741.
(7) Bunker, C. E.; Lawson, G. E.; Sun, Y. P. *Macromolecules* **1995**, *28*, 3744.
(8) Camp, A. G.; Lary, A.; Ford, W. T. *Macromolecules* **1995**, *28*, 7959.
(9) Sun, Y.-P.; Ma, B.; Bunker, C. E.; Liu, B. *J. Am. Chem. Soc.* **1995**, *117*, 12705.
(10) Cao, T.; Webber, S. E. *Macromolecules* **1996**, *29*, 3826.
(11) Sun, Y.-P.; Lawson, G. E.; Bunker, C. E.; Johnson, R. A.; Ma, B.; Farmer, C.; Riggs, J. E.; Kitaygorodskiy, A. *Macromolecules* **1996**, *29*, 8441.
(12) Bune, Ye. V.; Gromov, V. R.; Izumnikov, A. L.; Kardash, I. E. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; pp 1550−1560.
(13) Wang, C.; He, J.; Fu, S.; Jiang, K.; Cheng, H.; Wang, M. *Polym. Bull.* **1996**, *37*, 305.
(14) Dimitrijevic, N. D.; Kamat, P. V.; Fessenden, R. W. *J. Phys. Chem.* **1993**, *97*, 615.
(15) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Chem. Soc. Chem. Commun.* **1993**, 84.
(16) Walbiner, M.; Fischer, H. *J. Phys. Chem.* **1993**, *97*, 4880.
(17) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258.
(18) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; pp II/1−II/152.
(19) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661.
(20) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.
(21) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274.
(22) Lusignan, C. P.; Mourey, T. H.; Wilson, J. C.; Colby, R. H. *Phys. Rev. E* **1995**, *52*, 6271.
(23) Camp, A. G.; Ford, W. T.; Lary, A.; Sensharma, D. K.; Chang, Y. H.; Hercules, D. M.; Williams, J. B. *Fullerene Sci. Technol.* **1997**, *5*, 527.
(24) Stewart, D.; Imrie, C. T. *Chem. Commun.* **1996**, 1383.
(25) Jackson, C.; Frater, D. J.; Mays, J. W. *J. Polym. Sci., Part B: Polym Phys.* **1995**, *33*, 2159.
(26) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.
(27) D'Souza, F.; Caron, C.; Subramamian, R.; Kutner, W.; Jones, M. T.; Kadish, K. M. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; pp 768−778.
(28) Mourey, T. H.; Coll, H. *ACS Adv. Chem. Ser.* **1995**, *247*, 123.
(29) Mourey, T. H.; Balke, S. T. *ACS Symp. Ser.* **1993**, *521*, 180.
(30) Stockmayer, W. *J. Chem. Phys.* **1943**, *11*, 45
(31) Stockmayer, W. *J. Chem. Phys.* **1944**, *12*, 125.
(32) Zimm, B. H.; Stockmayer, W. *J. Chem. Phys.* **1949**, *17*, 1301.
(33) Osawa, S.; Osawa, E.; Harada, M. *J. Org. Chem.* **1996**, *61*, 257.
(34) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454.

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