Communications to the Editor

Free-Radical Polymerization of Methyl Methacrylate and Styrene with C_{60}

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The availability of C_{60} in gram quantities[1] has led to wide exploration of its chemical reactivity. Many types of polymers containing C_{60} have been prepared by attachment of C_{60} as a side chain to preformed polymers and by inclusion of C_{60} in the main chain,[2] via step-growth copolymerizations of a bisphenol derivative of C_{60},[3,4] nucleophilic additions of α,ω-diamino polyethers to C_{60},[5] addition of living polystyrene to C_{60},[6] cationic polyalkylation to form an insoluble network,[7] and copolymerization of C_{60} with *p*-xylylene to form an insoluble solid.[8] Cao and Webber[9] and Bunker, Lawson, and Sun[10] discovered that C_{60} copolymerizes with styrene in bulk and in solution by thermal self-initiation and by thermal initiation with azobis(isobutyronitrile) (AIBN) or dibenzoyl peroxide. Before their work was reported, we found that both styrene (S) and methyl methacrylate (MMA) in solution initiated by AIBN form polymers with C_{60} and that MMA gives higher yields and more thorough incorporation of C_{60}. The free-radical polymerizations are simple to perform, large amounts of C_{60} can be incorporated, and the polymers can be used to form coherent clear films. The polymers, however, are complex mixtures, and the properties of the highly functionalized C_{60} may be substantially altered from those of C_{60} and less substituted C_{60} derivatives.

In a typical polymerization, a sonicated solution of C_{60} (Hoechst, >97% C_{60}) in *o*-dichlorobenzene (DCB) was added to the monomer. The solution was heated to 70 °C under air without stirring (MMA) or 64 °C under nitrogen with stirring (S). A DCB solution containing 5 mol of AIBN/mol of C_{60} was added, and the solution was heated at 70 or 64 °C for 16−17 h. The solution was cooled and added dropwise to a tenfold excess of magnetically stirred hexane, diethyl ether, or methanol to precipitate the brown polymer, the mixture was filtered through a glass frit, and the solid was washed with methanol. The 5% and 10% C_{60} polymers contained material that passed through filters, and consequently the solid was precipitated by centrifugation, the liquid was decanted, and the precipitate was washed with methanol, sonicated, and centrifuged again. The 1% C_{60}PMMA and 1% C_{60}PS samples were reprecipitated into methanol; the 5% and 10% C_{60} polymers were not purified further. All samples were dried in vacuum at 80 °C. Compositions of the polymerization mixtures, yields, and descriptions of the polymers are reported in Table 1. Repetition of the 1% C_{60}PMMA synthesis twice under air, once under argon, and twice in evacuated sealed tubes produced yields of 67, 40, 62, 88, and 86%, respectively, with M_n in the range 16 200−19 500. We attribute the lower yields to evaporation of MMA during synthesis and to physical losses during filtration of the precipitated polymers.

Molecular weights of the polymers were analyzed by gel permeation chromatography (GPC) in tetrahydrofuran (THF) solutions with linear polystyrene standards. All of the PMMA samples and the 1% C_{60}PS sample were completely soluble in THF, but the 5% and 10% C_{60}PS samples were only partly soluble, and only the soluble part was analyzed. All C_{60} polymers were detected by UV absorption at 249 nm, where PS and C_{60} absorb, and the C_{60}PS samples also were detected at 400 nm, where only C_{60} absorbs. The UV−visible absorption spectra of the C_{60}PS samples were like those previously reported,[9,10] and in the spectra of the C_{60}-PMMA samples the absorbance decreased from a maximum at about 220 nm, with shoulders in the 250−340 nm range, to none at 820 nm, the longest wavelength measured. The molecular weight distributions of PS control samples, prepared under exactly the same conditions but containing no C_{60}, are narrower than those of the polymers containing C_{60}. The PS chromatograms detected at 249 nm have long retention time peaks of impurities that were not removed by two precipitations into methanol. These impurities contain no C_{60}, for they do not absorb at 400 nm. The starting C_{60} was not detected in any chromatogram. The molecular weight distributions of the PS samples detected at 400 nm are skewed to shorter retention time than those detected at 249 nm, indicating that the higher molecular weight components have higher C_{60} content. Number-average and weight-average molecular weights are reported in Table 2. Molecular weights of all samples are low because of the large amounts of AIBN employed (5 mol of AIBN/mol of C_{60}; Table 1), as shown by decreasing molecular weights of the PS control samples with increasing concentration of AIBN in the polymerization mixtures. The isolated yields of the control polymers were higher than those of the C_{60} polymers, consistent with less physical loss of low molecular weight components during isolation of higher molecular weight polymers.

Although all of the UV−visible spectra of the polymers in solution are qualitatively alike at >300 nm, there are marked differences in extinction coefficients, indicating that the C_{60} content increases more than in direct proportion to the amount of C_{60} used in the polymerization. If the 1% C_{60}PMMA sample is assumed to contain 1% C_{60} by weight and all samples have the same absorptivity per mole of C_{60} incorporated, the C_{60} contents of the other samples measured by absorbance at 400 nm are 5% C_{60}PMMA, 5.9%; 10% C_{60}PMMA, 26%; and 1% C_{60}PS, 5.7%.

NMR spectra of the polymers containing the lesser amounts of C_{60} are not significantly different from the spectra of the control samples. The ^{13}C NMR spectrum of the 10% C_{60}PMMA shown in Figure 1 is most

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Table 1. Conditions of Polymerization of C_{60} with MMA and Styrene

polymer	monomer (g)	AIBN (mg)	C_{60} (mg)	DCB (mL)	% yield[a]	appearance
1% C_{60}PMMA	2.44	33	24.4	5	67 (80)	light brown powder
5% C_{60}PMMA	2.50	143	125	8	65 (82)	dark brown chunks
10% C_{60}PMMA	2.51	285	250	16	5(57)	dark brown fine solid
1% C_{60}PS	2.44	28	24.5	5	6 (33)	light brown chunks
5% C_{60}PS	2.51	148	129	8	6 (39)	black fine solid
10% C_{60}PS	2.51	293	259	16	8 (4)	black fine solid

[a] Based on combined weight of monomer and C_{60}. Percent yields of control polymers prepared by identical procedures with no C_{60} are in parentheses.

Table 2. Properties of C_{60} Polymers

polymer[a]	M_n[b]	M_w[b]	T_g (°C)
1% C_{60}PMMA	18200	35600	117
control	*c*	*c*	120
5% C_{60}PMMA	4200	8000	112
control	*c*	*c*	119
10% C_{60}PMMA	2250	3200	*d*
control	*c*	*c*	115
1% C_{60}PS	9780	24700	99
control	16400	26700	95
5% C_{60}PS	900	1700	*d*
control	3960	5720	*c*
10% C_{60}PS	1810	2500	*d*
control	2980	3630	*c*

[a] Control polymers were prepared identically, except no C_{60} was used. [b] By GPC with UV detection at 249 nm. [c] Not measured. [d] No T_g was detected between 40 and 157 °C.

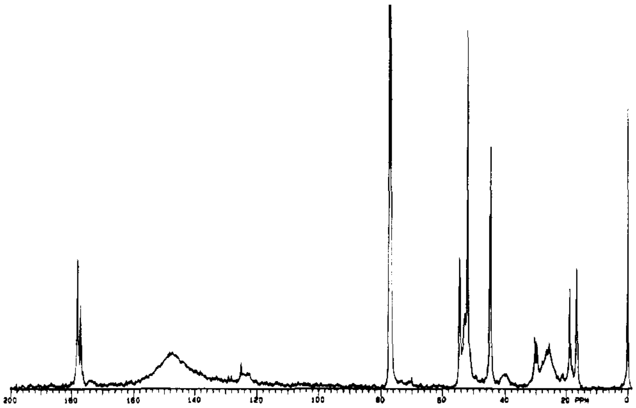

Figure 1. ^{13}C NMR spectrum of 10% C_{60}PMMA in $CDCl_3$ with tetramethylsilane reference. Signals due to C_{60} and AIBN carbon atoms are explained in the text. Signals due to PMMA are at 15−20, 44−56, and 175−180 ppm.

informative. In addition to signals due to PMMA, it contains broad bands at 22−32 ppm from methyl carbons of AIBN derivatives, 38−42 ppm from quaternary carbons of AIBN derivatives, 120−126 ppm from cyano carbons of AIBN derivatives, and 126−160 ppm from unsaturated carbon atoms of C_{60} derivatives. The band for saturated carbon atoms of substituted C_{60} is likely at 70−76 ppm. These assignments were confirmed by comparison with a spectrum of a sample prepared by reaction of the same amounts of C_{60} and AIBN in DCB in the absence of monomer.

Differential scanning calorimetric measurements of the glass transition temperatures of the polymers reported in Table 2 show that 1% C_{60} has only a small effect on T_g, and higher C_{60} contents make T_g indetectable. Thermal gravimetric analyses (TGA) of the PMMA samples in Figure 2 show that increasing amounts of C_{60} lower the temperature of onset of weight loss and increase the weight of residue remaining at high temperature, which must be mostly C_{60} or nonpolymeric C_{60} derivatives. The amount of residue from the 10% C_{60}-PMMA at 540 K correlates with the high C_{60} content indicated by its UV−visible and ^{13}C NMR spectra. The lower temperature onset of weight loss in TGA experiments may be due to homolysis of C_{60}-C_{60} bonds, which is the accepted interpretation for temperature-dependent ESR spectra of dimers of alkyl radical adducts of C_{60}.[11] Results of TGA of the PS samples (not shown) are similar to those of the PMMA samples.

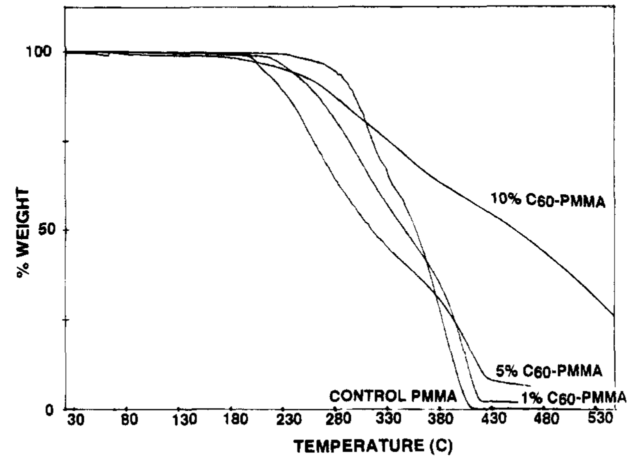

Figure 2. Thermogravimetric analyses of C_{60}PMMA samples heated under nitrogen at 40 °C min^{-1}.

Our polystyrenes containing C_{60} are similar to those of Cao and Webber[9] and of Bunker, Lawson, and Sun.[10] Like theirs, our THF-soluble polymers contain no unreacted C_{60}, have broad molecular weight distributions, have molecular weights that decrease with increasing amounts of C_{60}, and have UV−visible spectra indicative of mixtures of C_{60} derivatives. The weight percents of C_{60} in the polymers exceed those in the starting polymerization mixtures. MMA polymerizes to higher yield of more uniform C_{60}-containing polymers than does styrene. The 1% C_{60}PMMA sample forms a clear brown film when coated onto glass from THF solution, and THF solutions of 50/50 mixtures of the 5% C_{60}PMMA and 1% C_{60}PS with higher molecular weight PMMA and PS also form clear films.

We speculate that the polymers are formed by multiple additions of radicals to C_{60} to give mixtures having many different numbers of oligomeric chains bound to C_{60} and many constitutional isomers of multiply substituted C_{60} cores. Thus the C_{60} structures are more highly substituted than the so-called "flagellenes"[12] formed by addition of living anionic polystyrene to C_{60}. This interpretation is supported by the broad bands of signals from C_{60} and from AIBN fragments in the ^{13}C NMR spectrum. Multiple addition of radicals such as benzyl and *tert*-butyl to C_{60} is well known.[13-16] Rate constants for addition of alkyl radicals to C_{60} are reported to be 10^7-10^9 M^{-1} s^{-1},[17-20] much higher than rate constants for propagation during free-radical polymerization of styrene and of MMA. Consequently, the

C_{60} is consumed early in the polymerization, the C_{60} derivatives formed by radical addition react with more radicals to give multiply substituted C_{60} units, and longer PMMA and PS chains are formed only after the C_{60} is so highly substituted that rates of addition of radicals to the C_{60} units are slowed down. Termination would occur mainly by coupling of two C_{60} radicals, because the concentration of C_{60} radicals during polymerization is much higher than the concentration of monomer-ended radicals. Experiments to test mechanisms of polymerization and to determine better the structures of the polymers are in progress.

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References and Notes

(1) Kratschmer, W.; Lamb, L. D.; Fostiropaulus, K.; Huffman, D. *Nature* **1990**, *347*, 354.
(2) For reviews, see: (a) Geckeler, K. E. *Trends Polym. Sci.* **1994**, *2*, 355. (b) Hirsch, A. *Adv. Mater.* **1993**, *5*, 859.
(3) Shi, S.; Khemani, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656.
(4) Berrada, M.; Hashimoto, Y.; Miyata, S. *Chem. Mater.* **1994**, *6*, 2023.
(5) Manolova, N.; Rashkov, I.; Van Damme, H.; Beguin, F. *Polym. Bull.* **1994**, *33*, 175.
(6) Samulski, E. T.; DeSimone, J. M.; Hunt, M. O., Jr.; Menceloglu, Y. Z.; Jarnagin, R. C.; York, G. A.; Labat, K. B.; Wang, H. *Chem. Mater.* **1992**, *4*, 1153.
(7) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. *J. Am. Chem. Soc.* **1991**, *113*, 9387.
(8) Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977.
(9) Cao, T.; Webber, S. E. *Macromolecules* **1995**, *28*, 3741.
(10) Bunker, C. E.; Lawson, G. E.; Sun, Y. P. *Macromolecules* **1995**, *28*, 374.
(11) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454.
(12) Wignall, G. D.; Affholter, K. A.; Bunick, G. J.; Hunt, M. O., Jr.; Menceloglu, Y. Z.; DeSimone, J. M.; Samulski, E. T. *Macromolecules* **1995**, *28*, 6000.
(13) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.
(14) 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.
(15) McEwen, C. N.; McKay, R. G.; Larsen, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 4412.
(16) (a) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 3576. (b) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1425.
(17) Dimitrijevic, N. D.; Kamat, P. V.; Fessenden, R. W. *J. Phys. Chem.* **1993**, *97*, 615.
(18) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1993**, *84*.
(19) Walbiner, M.; Fischer, H. *J. Phys. Chem.* **1993**, *97*, 4880.
(20) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258.

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