J. Am. Chem. Soc. **1995**, *117*, 12705−12711 12705

All-Carbon Polymers (Polyfullerenes) from Photochemical Reactions of Fullerene Clusters in Room-Temperature Solvent Mixtures

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Received June 22, 1995[⊗]

Abstract: Polyfullerenes, which are polymers of covalently cross-linked fullerene molecules, are a new class of all-carbon polymeric materials in addition to graphite and diamond. The facile preparation of these materials can be accomplished by taking advantage of a unique property of the fullerenes C_{60} and C_{70}, namely that they form clusters in solvent mixtures consisting of fullerene-soluble and fullerene-insoluble components. The formation and properties of C_{60} and C_{70} clusters in toluene−acetonitrile mixtures are investigated. High molecular weight polyfullerenes are prepared from photochemical reactions of the fullerene clusters in carefully deoxygenated toluene−acetonitrile solutions at room temperature. The polymers are characterized by photon correlation spectroscopy of quasi-elastic light scattering, matrix-assisted laser desorption ionization time-of-flight mass spectroscopy, NMR, FT-IR, and optical spectroscopic methods.

Introduction

Since the development of methods for mass production of fullerene compounds, there has been great interest in the preparation and characterization of fullerene-based polymeric materials.[1,2] These materials can roughly be classified into two categories. One consists of copolymers in which fullerenes are part of the polymer structures,[3−14] and the other includes covalently linked fullerenes,[15−20] which we call polyfullerenes. As all-carbon polymers, polyfullerenes are structurally different from the other two polycarbon materials, graphite and diamond. Novel applications of polyfullerenes as a unique class of materials can be anticipated.

Preparation of polymeric materials through cross-linking between neighboring fullerene molecules in the solid state has been reported.[15,16,19,20] By irradiating oxygen-free, face-centered-cubic C_{60} films with visible or ultraviolet light, C_{60} molecules in the films are cross-linked into oligomers/polymers.[15] According to results from laser desorption mass spectroscopy, these oligomers/polymers in the phototransformed films consist of up to 21 C_{60} units.[21] The phototransformed films were also characterized using electron microscopy, thermal, and spectroscopic methods.[21−24] The same research group also reported[16] that a similar phototransformation of solid C_{70} films is considerably more difficult. It was suggested that the much lower phototransformation yield for solid C_{70} films is a result of a smaller number of $C=C$ double bonds that can participate in the cross-linking since a specific alignment of two neighboring C_{70} molecules is required.[16] A mechanism of [2 + 2] cycloaddition through the excited triplet states of the fullerenes was proposed for the phototransformation.[15,16,22] In addition, there have been several studies of metal fullerides,[17−20] in which high molecular weight polyanions were obtained.[20] The formation of polyanions was also explained by a [2 + 2] cycloaddition mechanism. It was argued[20] that the forbidden ground-state [2 + 2] cycloaddition for the neutral molecule[25] becomes thermally allowed for the singly charged fulleride anions. Theoretical calculations seem to support a likely involvement of a [2 + 2] cycloaddition mechanism in the cross-linking of two neighboring C_{60} molecules.[26] In this paper, we report a facile method for

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[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.

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photochemically preparing high molecular weight polyfullerenes in a room-temperature solution under oxygen-free conditions. The photopolymerization reactions can also be explained in terms of [2 + 2] cycloaddition through the excited triplet states of the fullerenes.

Recently, we discovered[27] that C_{70} exhibits dramatic solvatochromism in room-temperature solvent mixtures. Each of the mixtures consists of two solvents in which C_{70} has very different solubilities. A good example is mixtures of toluene and acetonitrile, which are C_{70}-soluble and C_{70}-insoluble, respectively. At a C_{70} concentration of 7 μM, there is no solution color change from toluene to toluene–acetonitrile mixtures with low acetonitrile compositions. However, when the acetonitrile volume fraction in the mixture is 70% and higher, the solution color becomes very different. The dramatic solvatochromism is due to the formation of microscopic aggregates or clusters of C_{70} molecules.[27] The C_{70} cluster solution is stable, showing no sign of precipitation after being stored in the dark for more than a year. It is also not damaged during deoxygenation by bubbling the solution with dry nitrogen gas for an extended period of time. The fullerene clusters are solidlike species, which can be used in the preparation of polyfullerenes. In the clusters, local concentrations of fullerene molecules are likely to be very high, amenable to polymerization through photochemical cycloaddition reactions. Thus, a carefully deoxygenated solution of fullerene clusters serves as a unique vehicle for an efficient photochemical preparation of high molecular weight polyfullerenes.

In the reported work, the formation and properties of C_{60} clusters in room-temperature solvent mixtures were studied in addition to further characterization of C_{70} clusters. High molecular weight polyfullerenes were prepared from photochemical reactions of C_{60} and C_{70} clusters in toluene–acetonitrile mixtures and characterized by photon correlation spectroscopy of quasi-elastic light scattering,[28–30] matrix-assisted laser desorption ionization time-of-flight mass spectroscopy, NMR, FT-IR, and optical spectroscopic methods.

Experimental Section

Materials. Fullerenes C_{60} (>99.9%) and C_{70} (>98%) were obtained from MER Co. Purities of the materials were verified using HPLC and ^{13}C NMR methods. Spectrophotometry grade toluene, acetonitrile, *o*-dichlorobenzene, carbon disulfide (CS_2), and dimethyl sulfoxide (DMSO) were obtained from Burdick & Jackson. The solvents were used without further purification. DMSO-d_6 containing 0.03% tetramethylsilane for NMR measurements was obtained from Cambridge Isotope Laboratories. Polystyrene standards for the calibration of the light-scattering instrument were obtained from Duke Scientific Co.

Measurements. Absorption spectra were obtained using Shimadzu UV-2101PC UV/vis and UV-3100 UV/vis/NIR spectrophotometers. A 1-cm optical path square cuvette and 5-cm optical path cylindrical cuvette were used.

A photochemical apparatus consisting of a 450-W xenon arc lamp (Spectral Energy) and an optical bench was used for photoirradiation. Cylindrical photochemical cells (50 and 100 mL) were employed. Larger-scale preparative photochemical reactions were carried out using an ACE-7861 type immersion-well photochemical reaction assembly (Ace Glass Inc.). The light source is a 450-W Hanovia medium pressure mercury lamp. The circulating cooling water jacket serves as a filter for absorbing near-IR irradiation of the lamp. The sample container has inlet and outlet openings for continuous bubbling of nitrogen gas during photoirradiation. A Pyrex glass filter and an aqueous $CuSO_4$ solution filter were used.

Proton and ^{13}C NMR measurements were performed on a Bruker 300-MHz NMR spectrometer. DMSO-d_6 was used as a solvent and tetramethylsilane was used as an internal standard.

Fullerene cluster and polymer size determinations were based on the method of photon correlation spectroscopy of quasi-elastic light scattering (PCS-QELS).[28–30] The technique of PCS-QELS, which has been used extensively to characterize particles and macromolecules in the size range from a few nanometers to a few microns, is based on correlating the fluctuations in the scattered light intensity. For macromolecule solutions, fluctuations about the average intensity of the scattered light are due to significant random or Brownian motion of the macromolecules. Since the random or Brownian motion is related to molecular diffusional properties, the principal quality measured by PCS-QELS is the translational diffusion coefficient D of the macromolecules. The effective diameter of the particles is calculated from D in terms of hydrodynamic equations.[30] Therefore, the calculated diameter is in fact the hydrodynamic diameter of the macromolecular species. For broad macromolecular size distributions, results from the method of PCS-QELS are intensity weighted. The intensity-averaged molecular size is generally larger than the weight-averaged molecular size for the same sample.

All PCS-QELS analyses were performed on a BI-90 Particle Sizer (Brookhaven Instruments Co.), which is equipped with a 5 mW, vertically polarized, He–Ne laser and a computer-controlled correlator. The instrument was operated in multiple sample time mode. In this mode the equivalent of several thousand linearly-spaced correlator channels is available, enabling the acquisition of a correlation function more fully representative of a broad size distribution. Measurements were carried out in a right-angle geometry, and the sample solution in a 1-cm cuvette was thermostated at 25 °C. An aqueous suspension of polystyrene particles (in the presence of NaCl) was used as a standard for the verification of instrument calibration. All solvents used in PCS-QELS analyses were repeatedly filtered through 0.4-μm filters. For the treatment of results in solvent mixtures, the required viscosity (η) and refractive index (n) values of the mixtures were calculated from those of the neat solvents,[31]

$$\ln \eta_{MIX} = x_1 \ln \eta_1 + x_2 \ln \eta_2 \qquad (1)$$

$$n_{MIX} = x_1 n_1 + x_2 n_2 \qquad (2)$$

where x represents mole fractions.

FT-IR spectra were obtained on a Nicolet Magna-IR 550 FT-IR spectrometer. Samples for measurements were mixed with carefully dried KBr solid, and the solid mixture was then made into pellets using a manual press. All measurements were carried out under the protection of dry nitrogen gas.

Matrix-assisted laser desorption ionization time-of-flight mass spectroscopic analyses were conducted on a Kratos Kompact-III mass spectrometer equipped with a nitrogen laser. α-Cyano-4-hydroxycinnamic acid was used as the matrix material.

Results and Discussion

C_{70} Clusters. C_{70} clusters were generated in a room-temperature toluene–acetonitrile solvent mixture with acetonitrile volume fraction x_{ACE} of 76% by rapidly pouring neat acetonitrile into a toluene solution of C_{70}. This is referred to as the "fast" method.[27] It is opposite to the "slow" method, in which acetonitrile is added to toluene drop by drop using a buret.[27] The C_{70} concentration in the solvent mixture is 1.4×10^{-5} M. As reported previously,[27] the solution color is reddish purple, different from that of monomeric C_{70} in neat toluene. The corresponding absorption spectra are shown in Figure 1.

The formation of C_{70} clusters was investigated by the method of photon correlation spectroscopy of quasi-elastic light scattering (PCS-QELS).[28–30] The results show that the average size

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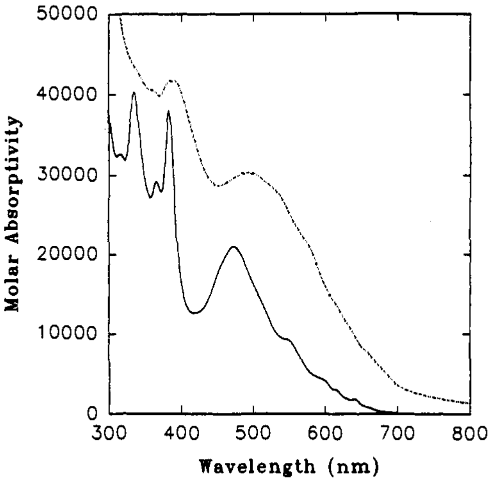

Figure 1. Absorption spectra of the C_{70} monomer in toluene (—) and the C_{70} clusters in a toluene–acetonitrile mixture with a C_{70} concentration of 1.4×10^{-5} M and acetonitrile volume fraction of 76% (-···-).

of the clusters is 186 nm, with a width of size distribution[32] of 134 nm. The cluster solution preparation and the PCS-QELS results are reproducible within experimental uncertainties.[33] The cluster solution is stable, showing no sign of precipitation over time. It is also stable with respect to deoxygenation by continuously bubbling dry nitrogen gas through the solution.

Polyfullerenes from C_{70} Clusters. A large volume (400 mL) of the C_{70} cluster solution in toluene–acetonitrile ($x_{ACE} = 76\%$) was obtained from a collection of small volumes of solutions that were generated using the "fast" method.[27] The use of a relatively small solution volume (50 mL) in each preparation is to ensure a reproducible execution of the "fast" method. Before photoirradiation, the cluster solution (50–100 mL per experiment) was deoxygenated thoroughly by purging with dry nitrogen gas for ~1 h in a glass bubbler, and then quickly transferred to a cylindrical photochemical cell. The solution was further bubbled with dry nitrogen gas in the photochemical cell, sealed, and then irradiated for ~48 h using a 450-W xenon arc lamp with a cylindrical water filter and a 360 nm glass sharp-cut filter. On a larger scale (400 mL per experiment), photoirradiation was carried out in an immersion-well photochemical reaction assembly. A cylindrical Pyrex glass filter and an aqueous $CuSO_4$ solution filter were used. During photoirradiation (~36 h), the deoxygenated solution in the reaction vessel was purged with a slow stream of dry nitrogen gas to prevent re-contamination by oxygen. The solution undergoes no significant color changes as a result of photoirradiation, except for a slight darkening. After evaporation of the solvents, the reaction mixture contained photoproducts that are insoluble in toluene. The photoproducts were isolated by repeatedly extracting the reaction mixture with toluene to remove unreacted C_{70}. The materials thus obtained are dark reddish brown solids, which are insoluble in common organic solvents such as chloroform, as well as fullerene solvents such as CS_2 and *o*-dichlorobenzene. However, the solids are somewhat soluble (~2 mg/mL) in DMSO, yielding a dark brown solution. The absorption spectrum of the photoproducts in DMSO is shown in Figure 2.

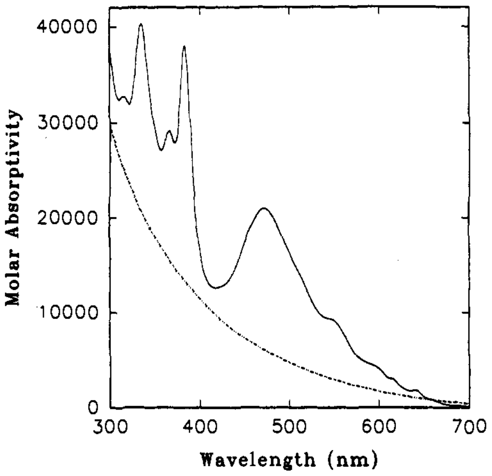

Figure 2. Absorption spectra of the C_{70} monomer in toluene (—) and the C_{70} polymers in DMSO (-···-). The molar absorptivities of the polymers are per C_{70} unit.

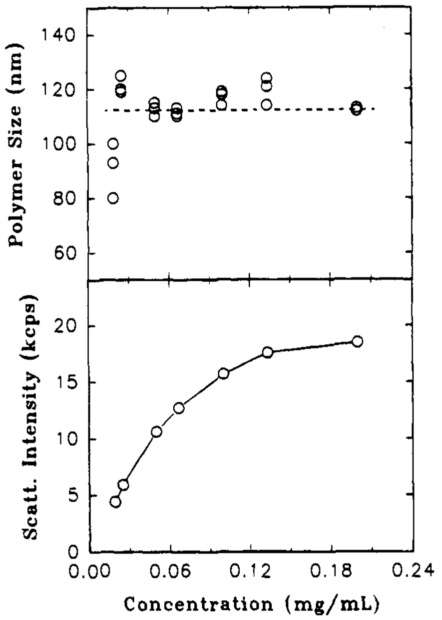

Figure 3. Results from PCS-QELS analyses of the C_{70} polymers in a DMSO solution (25 °C) as a function of the polymer concentration. The dashed line represents the average value.

Proton NMR measurements of the photoproducts in a DMSO-d_6 solution resulted in no meaningful signals. However, the ^{13}C NMR spectrum (44 000 scans) consists of an extremely broad peak in the 130–150 ppm region, consistent with the presence of fullerene polymers.[34]

The polymeric nature of the materials from photochemical reactions of C_{70} clusters was confirmed by PCS-QELS analyses.[28–30] In a solution prepared using carefully filtered DMSO, an average polymer size of 112 nm was found. Because the materials have absorption in the visible region, the light-scattering measurements were carried out using a relatively dilute solution (0.2 mg/mL). However, it is still possible to examine concentration effects by gradually diluting the sample solution up to an order of magnitude. As shown in Figure 3, observed average polymer sizes are essentially independent of concentration, indicating that the light scattering cannot be due to molecular aggregates.

Repeated efforts were made to analyze the polymeric materials using the matrix-assisted laser desorption ionization time-

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(32) BI-90 Particle Sizer uses a two-parameter lognormal distribution function to describe broad size distributions. The width of size distribution is defined as twice the standard deviation of the lognormal distribution. Since PCS-QELS is not considered as a particularly reliable method for the description of broad size distributions, the results of width distributions may be regarded as qualitative.

(33) The accuracy of the instrument is better than 2% on monodisperse samples. However, for broad distributions, the accuracy is likely to be much worse. The error limits are estimated to be ±9% on the basis of the results from series dilutions (Figures 3 and 9).

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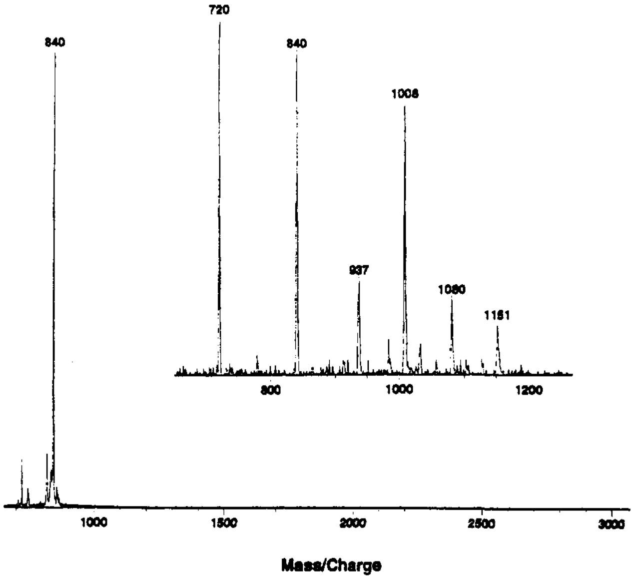

Figure 4. The result from MALDI-TOF analysis of the C_{70} polymers at high laser power (α-cyano-4-hydroxycinnamic acid as a matrix material). The insert is the result of toluene-extracted fullerene soot at low laser power. Under the experimental conditions, no signal was observed for the C_{70} polymers.

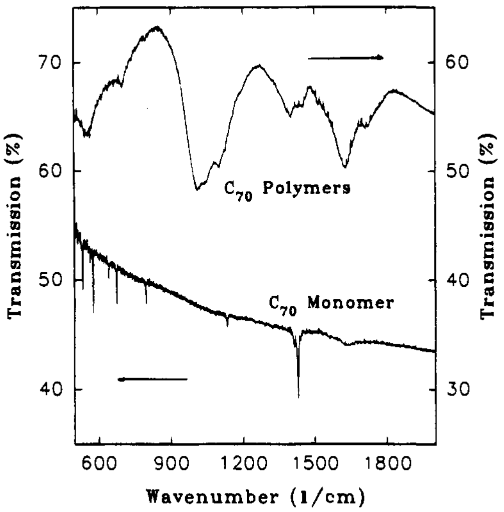

Figure 5. The FT-IR spectrum of the C_{70} polymers in KBr matrix. The spectrum of the C_{70} monomer is also shown for comparison.

of-flight (MALDI-TOF) mass spectroscopic method under different conditions. At low laser power, no signal was observed for the materials, while excellent spectra were obtained for extracted fullerene soot and for pure C_{70} (both as references) under the same experimental conditions (Figure 4). However, a weak C_{70} peak was observed at medium and high laser powers, despite the fact that the sample contains no C_{70} monomer (Figure 4). The presence or absence of the matrix material α-cyano-4-hydroxycinnamic acid had little effect on the results. It seems that the polymers have difficulty being desorbed and ionized without decomposing under the experimental conditions.

Because the formation of C_{70} clusters in toluene–acetonitrile mixtures at a C_{70} concentration of 1.4×10^{-5} M requires high acetonitrile compositions,[27] control experiments were carried out by photoirradiating C_{70} in toluene–acetonitrile mixtures with x_{ACE} less than 50%. There was no cluster formation, and photoirradiation resulted in no meaningful reactions.

The FT-IR spectrum of the polymeric materials in a KBr matrix is very different from that of C_{70} monomer. As shown in Figure 5, the IR bands of the polymers are rather broad. The spectrum is not affected by the way in which the sample pellet is prepared. For comparison, a sample was prepared by depositing the polymeric materials on the surface of a KBr plate. The FT-IR spectrum remains the same as that obtained in a KBr matrix. It has been reported[16] that materials consisting of cross-linked C_{70} molecules can be obtained from phototransformation of solid C_{70} films. However, because of extremely low transformation yields, the FT-IR spectrum of the solid C_{70} films that were photoirradiated for 10 days is still dominated by unreacted C_{70}.[16] The signals due to cross-linked C_{70} molecules in the films are rather weak, making a quantitative comparison with the result in Figure 5 somewhat difficult. Nevertheless, a common feature seems to be a broad peak around 1050 cm^{-1}, which was used as an indicator for the progress of phototransformation.[16] The spectrum of the polymeric materials also shows strong IR absorption in the 1300–1750 cm^{-1} region (Figure 5). The apparent difference between the spectrum shown in Figure 5 and the spectrum of phototransformed solid C_{70} films is at least partially due to the fact that the molecular weight of the polyfullerenes obtained from photoirradiation of C_{70} clusters in solution is likely to be much larger than that of the materials generated from phototransformation of solid C_{70} films.

C_{60} Clusters. The behavior of C_{60} in toluene–acetonitrile mixtures is in many ways similar to that of C_{70}. As the composition of solvent mixtures varies, the C_{60} solution also undergoes dramatic solvatochromic changes, and the changes are strongly dependent on the C_{60} concentration. The solvatochromism is similarly attributed to the formation of C_{60} clusters in the solvent mixtures. On the basis of extensive investigations on the formation and properties of C_{70} clusters,[27] it is established that stable cluster solutions can be generated only by the "fast" method. The "slow" method results instead in a precipitation of the fullerene molecules from the solution.[27] Therefore, only the C_{60} cluster solutions obtained by the "fast" method were examined in detail because stable solutions are required in the photochemical preparation of polyfullerenes. However, even by the "fast" method, the clustering behavior of C_{60} in toluene–acetonitrile mixtures seems somewhat more complicated than that of C_{70}.

Solutions of C_{60} in toluene–acetonitrile mixtures were prepared using the "fast" method. The C_{60} concentration in these solutions was varied from 5×10^{-6} to 1×10^{-4} M. For each C_{60} concentration, a series of toluene–acetonitrile mixtures of different compositions was used. At a C_{60} concentration of 5×10^{-6} M and x_{ACE} of 70% and less, the solution is almost colorless because of the low concentration and the low molar absorptivity of C_{60} monomer. The absorption spectrum remains the same as that of C_{60} in neat toluene. However, as x_{ACE} is increased, solvatochromic changes become evident. At x_{ACE} of 90%, the solution color becomes faint yellow green, with a slightly cloudy appearance. The results are reproducible. At a higher C_{60} concentration of 1×10^{-5} M, the onset of solvatochromic changes is at x_{ACE} of 70% or so. The solution at this solvent composition has a faint peach color, different from the purple color of C_{60} in neat toluene and in mixtures with less acetonitrile. At an even higher C_{60} concentration of 1×10^{-4} M, changes in solution color and in the absorption spectrum can be observed at x_{ACE} of only 40%. A systematic comparison of the formation of C_{60} clusters under different conditions is summarized in Table 1. The results indicate that the threshold x_{ACE} value for the observation of solvatochromic changes decreases with increasing C_{60} concentrations. This is similar to the trend observed in the formation of C_{70} clusters.

The stability of the cluster solutions varies with C_{60} concentration and x_{ACE}. For a solution that is called stable, there is no precipitation of solid from the solution over an extended

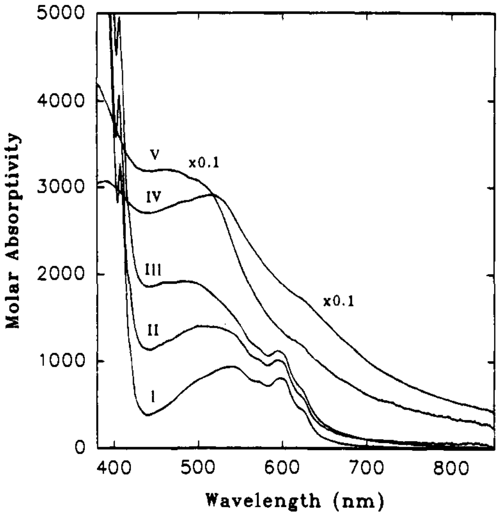

Figure 6. Absorption spectra of the C_{60} monomer (I) and the C_{60} clusters in toluene–acetonitrile mixtures with C_{60} concentrations of 5×10^{-6} (IV, $x_{ACE} = 90\%$), 1×10^{-5} (V, $x_{ACE} = 80\%$), 5×10^{-5} (II, $x_{ACE} = 50\%$), and 1×10^{-4} M (III, $x_{ACE} = 40\%$).

Table 1. Formation and Characteristics of C_{60} Clusters in Toluene–Acetonitrile Mixtures

$[C_{60}]$ M	x_{ACE}, %	observation
5×10^{-6}	70	characteristics of monomer solution
	80	very light pink solution, precipitate
	90	faint yellow green solution, slightly cloudy, no precipitate
1×10^{-5}	60	characteristics of monomer solution
	70	faint peach solution, precipitate
	80	yellow orange solution, slightly cloudy, no precipitate
5×10^{-5}	40	characteristics of monomer solution
	50	red purple solution, clear, no precipitate
	60	amber solution, cloudy, precipitate
1×10^{-4}	30	characteristics of monomer solution
	40	red purple solution, clear, no precipitate
	50	amber solution, cloudy, precipitate

period of time. As summarized in Table 1, a stable solution of C_{60} clusters is typically obtained at a solvent composition close to the threshold for solvatochromic changes. However, the stable solutions corresponding to different C_{60} concentrations have somewhat different properties (Table 1). Their absorption spectra (Figure 6) differ not only in the profiles but also in the absorptivities. For a given stable cluster solution, no visible changes with time were observed. As shown in Figure 7, the absorption spectrum of the solution with C_{60} concentration of 1×10^{-4} M and x_{ACE} of 40% remains essentially unchanged after the solution is stored in the dark for more than 24 h.

The C_{60} clusters were characterized by the PCS-QELS method.[28-30] Since the particle size distribution is time-dependent in unstable solutions, PCS-QELS analyses were performed only on the stable cluster solutions. As shown in Table 2, the average sizes of C_{60} clusters generated under different conditions fall in the range of 140 to 270 nm. The somewhat larger cluster size observed for the solution with a C_{60} concentration of 1×10^{-5} M and $x_{ACE} = 80\%$ is consistent with the fact that the solution appears slightly cloudy (Table 1).

Polyfullerenes from C_{60} Clusters. Two cluster solutions were used for photochemical reactions. One is a solution with a C_{60} concentration of 1×10^{-5} M and $x_{ACE} = 80\%$ (referred to as the dilute solution), and the other is a solution with a C_{60} concentration of 1×10^{-4} M and $x_{ACE} = 40\%$ (referred to as the concentrated solution). These C_{60} cluster solutions are stable, showing no precipitation over an extended period of time. They are also stable with respect to deoxygenation by continuously bubbling dry nitrogen gas through the solutions. Photochemical reactions were carried out in the immersion-well assembly. In each experiment, 400 mL of solution was used. As in the reactions of C_{70} clusters, the large volume of solution was obtained from a collection of many small volumes of solutions prepared using the "fast" method. Before photoirradiation, the solution was purged thoroughly with dry nitrogen gas for ~1 h in a glass bubbler. Re-contamination of oxygen during photoirradiation was prevented by continuously purging the deoxygenated solution with a slow stream of dry nitrogen gas. For both the dilute and the concentrated solutions, the photoirradiation time is ~30 h.

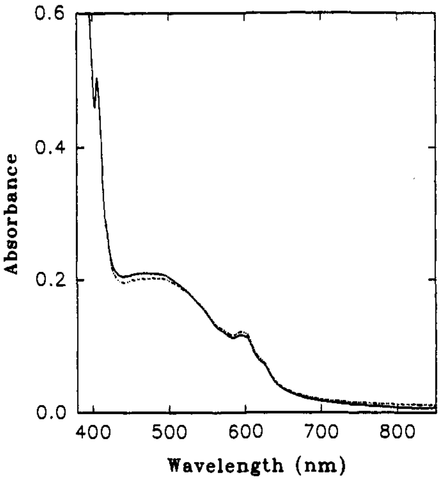

Figure 7. Absorption spectra of the C_{60} clusters in a toluene–acetonitrile mixture with a C_{60} concentration of 1×10^{-4} M and $x_{ACE} = 40\%$ (freshly prepared solution (—) and after the solution is stored in the dark for more than 24 h (···)).

The photoproducts from reactions of C_{60} clusters were isolated by repeatedly extracting the reaction mixtures with toluene. The dark reddish brown solid materials left behind are insoluble in common organic and so-called fullerene solvents, such as chloroform and *o*-dichlorobenzene. Although the materials are also slightly soluble in DMSO, they are inhomogeneous as far as solubility in DMSO is concerned. Unlike the polyfullerenes from C_{70} clusters, the materials from C_{60} clusters consist of two or more fractions, one of which has no solubility in DMSO. The absorption spectra of the DMSO-soluble fractions of the materials derived from two different C_{60} cluster solutions are shown in Figure 8. These solutions were also used in the determination of polymer sizes by the method of PCS-QELS.[28-30] The average sizes of the polyfullerenes obtained from photochemical reactions of the dilute and the concentrated C_{60} cluster solutions are close (Table 2). As shown in Figure 9, the PCS-QELS results are also independent of concentration, indicating that the light scattering is not due to aggregates of the materials as a result of their limited solubility in DMSO. The DMSO-insoluble fraction probably consists of even larger polymers and/or polymers with somewhat different three-dimensional structures.

Results from MALDI-TOF analyses of the polyfullerenes from C_{60} clusters are basically the same as those of polyfullerenes from C_{70} clusters. The only meaningful signal is a C_{60} peak.

The FT-IR spectra of the polyfullerenes from the two different C_{60} cluster solutions (the dilute and the concentrated) are similar (Figure 10). In the low-frequency region (450–800 cm^{-1}), they both have features comparable to those found in the spectrum of phototransformed solid C_{60} films.[15] However, a major difference is a broad band at ~1050 cm^{-1} in the spectrum of

Table 2. PCS-QELS Results of C_{60} Clusters in Toluene–Acetonitrile Mixtures and the Polyfullerenes Prepared from the C_{60} Clusters

	soln with $[C_{60}] = 5 \times 10^{-6}$ M and $x_{ACE} = 90\%$	soln with $[C_{60}] = 1 \times 10^{-5}$ M and $x_{ACE} = 80\%$	soln with $[C_{60}] = 5 \times 10^{-5}$ M and $x_{ACE} = 50\%$	soln with $[C_{60}] = 1 \times 10^{-4}$ M and $x_{ACE} = 40\%$
		Clusters		
av size (nm)[a]	217	269	158	143
size distribution (nm)[32]	67	77	124	98
scattering inten (kcps)	177	202	30	73
		The Corresponding Polyfullerenes in DMSO		
av size (nm)[a]		156		163
size distribution (nm)[32]		61		70
scattering inten (kcps)		400		175

[a] The error limits are estimated to be ±9%.[33]

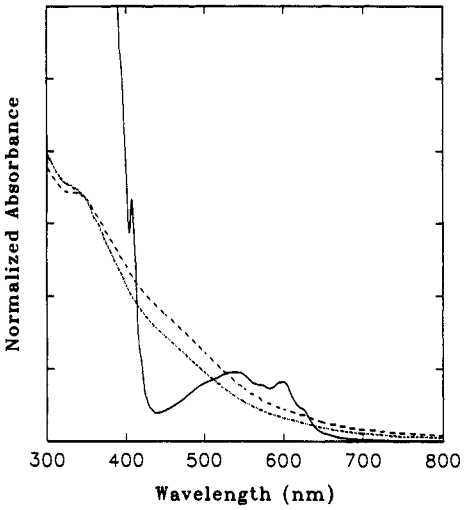

Figure 8. Absorption spectra of the C_{60} monomer in toluene (—) and the C_{60} polymers, which were prepared photochemically from two different C_{60} cluster solutions (the dilute (- - -) and the concentrated (-⋯-)), in DMSO.

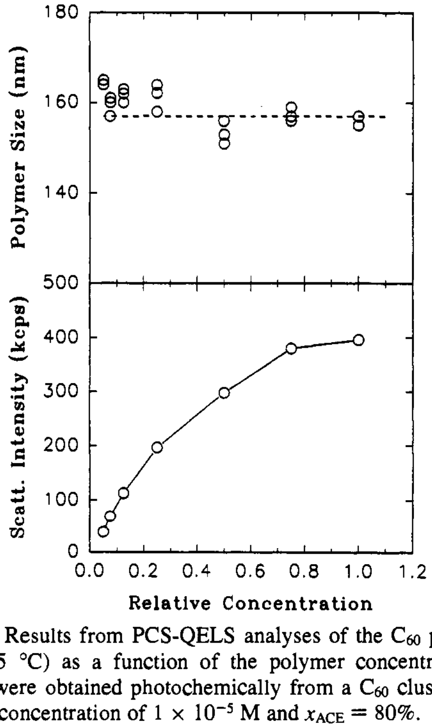

Figure 9. Results from PCS-QELS analyses of the C_{60} polymers in DMSO (25 °C) as a function of the polymer concentration. The polymers were obtained photochemically from a C_{60} cluster solution with a C_{60} concentration of 1×10^{-5} M and $x_{ACE} = 80\%$. The dashed line represents the average value.

the polyfullerenes. This band is not found in the spectrum of phototransformed solid C_{60} films. It is interesting that broad IR bands at similar frequencies are also observed in the spectra of the polyfullerenes from C_{70} clusters (Figure 5) and the spectrum of phototransformed solid C_{70} films.[16]

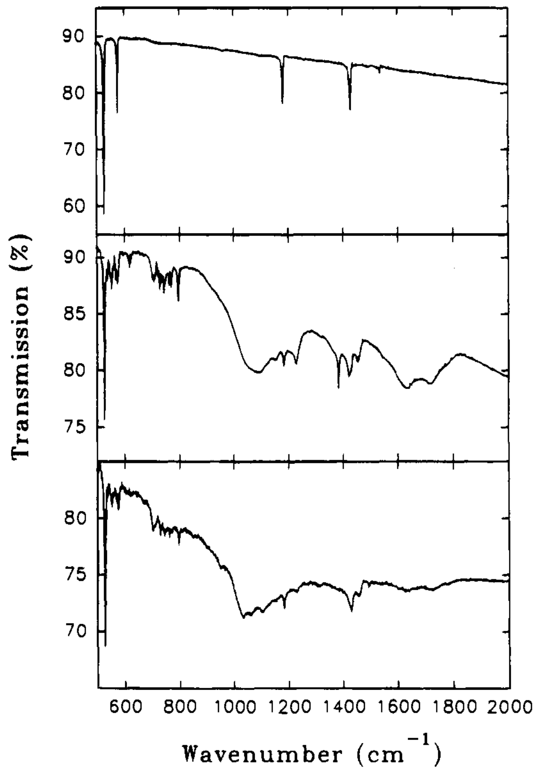

Figure 10. The FT-IR spectra of the C_{60} monomer (top) and the C_{60} polymers prepared photochemically from two different C_{60} cluster solutions (the dilute (middle) and the concentrated (bottom)).

Clusters, Reactions, and Polyfullerenes. The formation of clusters in solvent mixtures is a somewhat unique property of fullerene molecules. A microstructure conceptually similar to that of a micelle has been proposed for the clusters.[27] There seems to be a general tendency for fullerene molecules to aggregate in solutions. Slow aggregation of C_{60} in a room-temperature benzene solution has been reported.[35] However, while the cluster formation discussed here might be a reflection of such a general tendency, the critical factor is the specific environment in the solvent mixtures. In this regard, fullerene cluster formation in solvent mixtures is fundamentally different from the slow aggregation of C_{60} in a fullerene-soluble solvent like benzene. The fullerene clusters formed in solvent mixtures are much more stable with respect to physical disturbances such as shaking and stirring than the aggregates in a fullerene-soluble solvent.[36]

The photochemical reaction of fullerene clusters most likely follows the same mechanism as in the phototransformation of solid fullerene films. The cross-linking of fullerene molecules is assumed to occur through photochemical [2 + 2] cycload-

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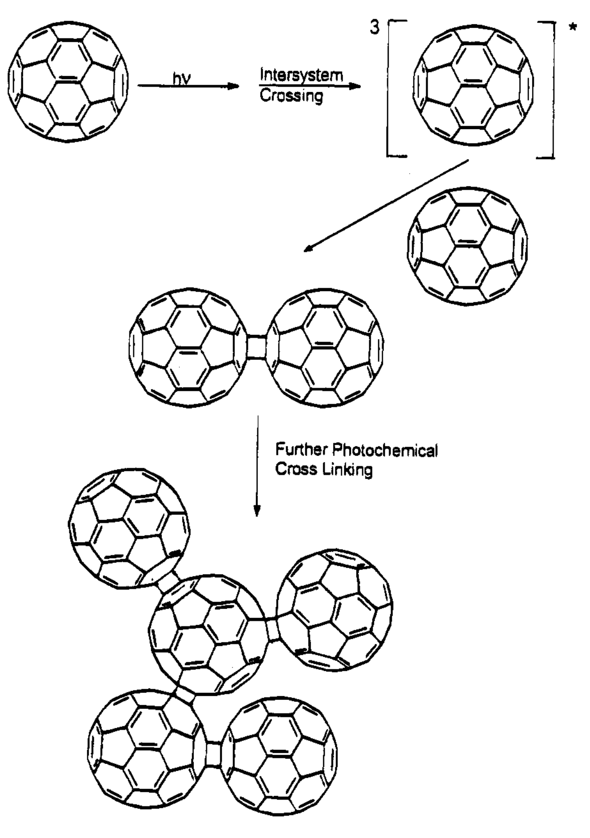
(36) The C_{60} aggregates in benzene solution can be dispersed simply by shaking the solution by hand.[35]

Scheme 1



dition reactions[25,37] in the excited triplet states of the fullerenes[15,16,22] (Scheme 1). Experimental evidence for the [2 + 2] cycloaddition mechanism in the cross-linking of fullerene molecules includes results from X-ray and Raman studies. The X-ray diffraction of the solid C_{60} films is altered upon phototransformation.[15,16] The lattice contraction in the phototransformed films is probably associated with decreased interfullerene distance, suggestive of chemical bonding.[15,16] Raman scattering studies of solid C_{60} films clearly indicate that phototransformation introduces a new mode at 118 cm^{-1}, which was identified with the covalent bonds between adjacent fullerene molecules.[16,22] The involvement of fullerene excited triplet states is supported by the fact that the photopolymerization does not occur in air-saturated fullerene cluster solutions. The excited singlet state lifetimes of C_{60} and C_{70} are ~1.2 ns and ~660 ps, respectively.[38] These short lifetimes are due to the rapid and efficient intersystem crossing to form excited triplet states. The triplet states of C_{60} and C_{70} are much longer-lived (40–50 μs),[39] so that quenching due to dissolved oxygen is substantial.

The polyfullerenes prepared photochemically from fullerene cluster solutions are high molecular weight polymers according to PCS-QELS analyses.[28–30] Although the fullerene clusters can be regarded as solidlike species, the environment surrounding a fullerene molecule in the clusters must be fundamentally different from that in the solid films. Limited diffusional freedom is likely to be preserved in the clusters. Thus, photochemical [2 + 2] dimerization as an elemental step in the formation of polyfullerenes from fullerene clusters may have different characteristics from that in the phototransformation of solid fullerene films. It may not require the same specific alignment of parallel double bonds on neighboring fullerene molecules (less than 4.2 Å separation) as in the phototransformation. Mobility of the clusters in solution also allows photoirradiation from different angles. These factors should facilitate the formation of high molecular weight polyfullerenes. The yields for the photochemical preparation of polyfullerenes from fullerene clusters are significant. Under the experimental conditions discussed above, the overall yield for polyfullerenes from the C_{70} cluster solution is ~20%, and the yields for polyfullerenes from the dilute and the concentrated C_{60} cluster solutions are ~70% and ~25%, respectively. Even without further optimization, photoirradiation of fullerene cluster solutions can be used as a relatively simple method for the preparation of bulk quantities of polyfullerenes.

Structures of the polymers are probably random. There seems to be no fundamental differences between the polymers generated from C_{60} and C_{70} clusters. The preparation of polyfullerenes from C_{70} clusters is not any more difficult than the preparation from C_{60} clusters. The results do not necessarily contradict the proposal that C_{70} is less reactive than C_{60} for photopolymerization in solid films.[16] The argument that the photochemical cycloaddition requires a specific alignment of neighboring C_{70} molecules is not applicable to the reactions of C_{70} clusters. The environment surrounding a C_{70} molecule in the clusters is flexible, so that the reactions are not subject to the kind of constraints found in the solid C_{70} films.

An interesting conclusion from the PCS-QELS results is that the polyfullerenes and the clusters from which the polymers are prepared have comparable sizes (Table 2). It seems to suggest that the photopolymerization is primarily due to intracluster reactions. There is also evidence indicating that the integrity of a cluster is largely preserved during photoirradiation. The small amount of precipitates found at the bottom of the reaction vessel after photoirradiation was identified as unreacted fullerenes. The polymeric materials in photoirradiated cluster solutions, though insoluble in toluene and acetonitrile, do not precipitate out of the solution even in a moderate centrifuge field of 3600 rpm for 10 min. The result supports an argument that the microstructures of the cluster solution before and after polymerization through photoinduced cross-linking of fullerene molecules are largely unchanged. In addition, the correlation between the sizes of fullerene clusters and those of the polyfullerenes that are prepared from the clusters offers an opportunity to manipulate the molecular weight and weight distribution of the polymers. Such investigations are in progress.

Polyfullerenes as a new class of all-carbon polymeric materials may find valuable applications in a number of fields. Their potential uses as molecular conductors, nonlinear optical materials, and hydrogen storage systems are being investigated.

Acknowledgment. We thank Dr. Alex Kitaygorodskiy for assistance in NMR measurements, and Professor Garth Spencer for comments on the application of the PCS-QELS technique. Financial support from the National Science Foundation (CHE-9320558), and in part from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Support from the Department of Energy through DoE/EPSCoR cooperative agreement DE-FG02-91ER75666 for the publication cost is also acknowledged.

JA952036A

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