Articles

Polyelectrolyte-Containing Fullerene I: Synthesis and Characterization of the Copolymers of 4-Vinylbenzoic Acid with C$_{60}$

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Polymerization of 4-vinylbenzoic acid in the presence of C$_{60}$ using free radical initiator resulted in covalent incorporation of C$_{60}$ in the polymer structure. Incorporation of the C$_{60}$ moieties in the polymer was established by IR, NMR, and UV–vis spectroscopy. The solution UV–vis spectra of these C$_{60}$-containing copolymers appear to be dominated by scattering, obscuring specific electronic excitation features associated with the fullerene. UV–vis spectral analysis of filtrate fractions collected using filters of varying pore sizes indicates that polymers form microgels with polydisperse particle sizes (micron to submicron dimensions) in solution that extensively scatter at shorter wavelengths. Differences in the fluorescence properties of the filtered fractions and unfiltered samples were observed. Furthermore, fluorescence emission spectra of a copolymer showed wavelength-dependent behavior. Polyelectrolyte behavior of these copolymers was studied by concentration dependent viscosity changes of the polymers in aqueous NaOH solutions of varying ionic strength. These copolymer microgels formed stable monolayers at the air–water interface of a Langmuir–Blodgett film balance. Solubilization of these polymers in dilute alkali solution offers a novel route to prepare fullerene-containing polyelectrolytes.

Introduction

Unique material properties, viz., superconductivity, ferromagnetism, nonlinear optical properties, and biological activity, exhibited by fullerene (C$_{60}$) based functional materials has led to intense research efforts in the chemistry of fullerene in recent years.[1–3] Diverse chemical reactivity of the C$_{60}$ molecule toward a number of reagents provides the framework in establishing the foundation of chemical derivatization of organo-fullerenes.[4] Fullerene units tethered to polymer chains have been considered to be particularly interesting. Incorporation of C$_{60}$ molecules into macromolecular architecture provides an attractive opportunity to combine the unique electronic and optical properties of fullerene with superior physicomechanical characteristics of polymers.[5] Research efforts toward synthesizing polymeric fullerene has predominantly involved tagging of C$_{60}$ molecules to preformed functional polymers through chemical modification. Using this protocol, several interesting polymer structures (including dendrimers) bearing C$_{60}$ units have been synthesized.[6] Another reported approach to obtain polymeric fullerene is the synthesis of fullerene-containing vinyl monomers and their subsequent polymerization.[7]

The versatile feature of the fullerene molecule is its ability to undergo addition reactions across its double bonds, which forms the principal basis for the organic chemistry of fullerene.[8] This implies that the double bonds of fullerene molecules can be utilized for linking with free radically grown vinyl polymer chains (i.e., C$_{60}$ molecule acts as a comonomer), thus offering an expeditious route for the synthesis of fullerene-containing polymers. This principle has in fact been utilized recently to synthesize polystyrene and poly(methyl

[†] Department of Chemistry.
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(1) Fischer, J. E.; Heiney, P. A.; Smith, A. B., III. *Acc. Chem. Res.* **1992**, *25*, 112.
(2) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
(3) Nakamura, E.; Tokuyama, H.; Yamago, S.; Shiraki, T.; Sugiura, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2143.
(4) (a) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157. (b) Hirsch, A. *Chemistry of Fullerenes*; Thieme: New York, 1994.
(5) (a) Hirsch, A. *Adv. Mater.* **1993**, *5*, 859. (b) Fischer, J. E. *Science* **1994**, *264*, 1548. (c) Chiang, L. Y.; Wang, L. Y. *Trend. Polym. Sci.* **1996**, *4*, 298.

(6) (a) Geckeler, K. E.; Hirsh, A. *J. Am. Chem. Soc.* **1993**, *115*, 3850. (b) Guhr, K. I. Greaves, M. D. Rotello, V. M. *J. Am. Chem. Soc.* **1994**, *116*, 5997. (c) Hawker, C. J. *Macromolecules* **1994**, *27*, 4836. (d) Liu, B.; Bunker, C. E. Sun, Y.-P. *Chem. Commun.* **1996**, 1241. (e) Wooley, K. L.; Hawker, C. J.; Frechet, J. M. J.; Wudl, F.; Srdanov, G.; Shi, S.; Li, C.; Kao, M. *J. Am. Chem. Soc.* **1993**, *115*, 9836.
(7) Zhang, N.; Schricker, S. R.; Wudl, F.; Prato, M.; Maggini, M.; Scorrano, G. *Chem. Mater.* **1995**, *7*, 441.
(8) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.

methacrylate) containing C_{60} units in the polymer chain.[9] These copolymers were considered to be soluble polymers possessing either linear or branched chain architectures. These C_{60}-containing vinyl copolymers were characterized by determination of their molecular mass by GPC as well as their spectral and thermal analyses.

As part of our ongoing research program on molecular architecture of novel polymers possessing interesting electronic and optical properties, we have been interested in designing fullerene-based functional polymers that possess interesting electronic properties and can be incorporated into prototype device structures.[10,11] Toward this end, we set out to copolymerize 4-vinylbenzoic acid (VBA) with C_{60} to obtain fullerene-containing polycarboxylic acids. These C_{60}-containing polycarboxylic acids can be readily neutralized with dilute alkali solution offering fullerene-containing anionic polyelectrolytes. We carried out systematic molecular characterization of these polymers to establish covalent incorporation of C_{60} units in the polymer chain. During analyses of these polycarboxylic acids we realized that although these copolymers form visually clear solutions, they are in fact solublized microgel dispersions. While these microgels are visually clear, they are large enough to significantly scatter UV and near visible radiation. Formation of microgel was not unique to this monomer system, and careful analyses revealed that earlier reported C_{60}-styrene copolymers,[9] obtained by free radical copolymerization, are in fact microgels. Furthermore, all these copolymers were contaminated with certain amounts of homopolymers of the vinyl comonomers which can be selectively removed. As a result of microgel formation and homopolymer contamination, characterization of these C_{60}-based copolymers is not a trivial problem. The presence of such contaminants may have serious consequences on the copolymers overall molecular and materials properties. To characterize these copolymers as precisely as possible, we carried out a systematic fractionation of the microgels and analyzed the electronic and fluorescence spectra of different fractions. Results on thermogravimetric analysis of the copolymers have been interpreted in light of the microgel formation. These fullereno-polycarboxylic acid microgels formed monolayers as is evident from their LB study. Results on these carefully performed studies are reported in this paper.

Experimental Section

Materials. Unless stated otherwise, all the solvents and reagents were commercially available guaranteed (G. R.) reagent grade obtained from Aldrich Chemicals and were purified by standard methods of purification prior to use. C_{60} fullerene was obtained from SES Research, Houston, with 99.9% purity. VBA was synthesized by following the reported procedure.[12]

(9) (a) Cao, T.; Webber, S. E. *Macromolecules* **1995**, *28*, 3741. (b) Camp, A. G.; lary, A.; Ford, W. T. *Macromolecules* **1995**, *28*, 7959. (c) 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. (d) Ford, W. T.; Graham, T. D.; Mourey, T. H. *Macromolecules* **1997**, *30*, 6422.

(10) (a) Chen, J. I.; Marturunkakul, S.; Li, L.; Jeng, R. J.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1993**, *26*, 7379. (b) Kim, W. H.; Bihari, B.; Moody, R.; Kodali, N. B.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 642. (c) Li, L.; Chen, J. I.; Marturunkakul, S.; Kumar, J.; Tripathy, S. K. *Opt. Commun.* **1995**, *116*, 421.

Instrumentation and Analyses. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 250 spectrometer operating at 250 MHz for ^{1}H and 75 MHz for ^{13}C nuclei. Chemical shift values reported are relative to tetramethylsilane (TMS) as the internal reference. Infrared spectra were recorded using a Perkin-Elmer 1720 spectrophotometer. Electronic absorption spectroscopic measurements were carried out with a Perkin-Elmer Lambda-9 UV-vis−near-IR spectrophotometer. Thermal transitions of the polymers were assessed using a Perkin-Elmer DSC-7 differential scanning calorimeter. In all cases, the heating and cooling rates were 20 °C/min. Thermal degradation patterns of the polymers were studied using a TA Instruments TGA-2950 thermogravimetric analyzer. The samples were heated at a rate of 20 °C/min under a nitrogen atmosphere. Fluorescence emission spectra were recorded on a SLM 8100 spectrofluorimeter. A 10-mm square cell was used for the fluorescence measurements with a solution optical density smaller than 0.1. A computer-controlled Lauda film balance was used to prepare monolayers of these polymers at the air−water interface. The concentration of the polymer solutions was ∼0.3 mg/mL in a mixture of DMF and chloroform (2:8, v/v). The viscosity of the polymer solution was measured as a function of dilution and salt concentration using an Ubbelohde Canon type viscometer at 20 °C.

Polymerization and Workup. Appropriate amounts of VBA, C_{60}, and 2,2′-azobis(isobutyronitrile) (AIBN) were dissolved in *o*-dichlorobenzene, and the solutions were bubbled with argon for 30 min. Subsequently, the polymerization mixtures were heated to 70 °C and stirred at this temperature for 24 h under a positive pressure of argon. Formation of polymer was evident from its precipitation from the reaction medium. After 24 h, the reaction mixture was cooled to room temperature. After decanting the solvent, the residue was dissolved in methanol, filtered, and precipitated into excess diethyl ether. The process was repeated three times. Finally, the polymer was dissolved in a 0.1 M aqueous NaOH solution, filtered through a filter paper, and acidified with dilute HCl to pH 2.0 to precipitate the polymer. It was filtered, washed with distilled water, and dried in a vacuum oven at 50 °C to a constant weight.

Fractionation of Copolymers. Dilute methanolic solution of the copolymers were filtered successively through membrane filter units of different pore diameters (10, 0.45, and 0.2 μm). Polymers retained on the filters were redissolved in methanol, and the solvent was subsequently evaporated to obtain the solid polymer. Similarly, the filtrates were also evaporated to isolate the polymer fractions. Different fractions were finally dried in a vacuum oven at 50 °C.

Results and Discussion

Synthesis and Molecular Characterization. As alluded to in the Introduction, addition to various reactive species is the principal reaction involving fullerene molecules.[8] Like styrene derivatives, the C_{60} molecule possesses the propensity to undergo addition reactions with anions and free radicals.[13] The knowledge of the adduct formation of C_{60} with free radicals has been the motivation of utilizing it as a comonomer for copolymerization with vinyl monomers. With AIBN as the free radical initiator, the copolymerization reaction was attempted. After dissolving appropriate amounts of C_{60}, VBA, and AIBN in *o*-dichlorobenzene, polymerization reactions were carried out at 70 °C in

(11) Kuo, C. S.; Wakim F. G.; Sengupta S. K.; Tripathy, S. K. *Solid State Commun.* **1993**, *87*, 115.

(12) Letsinger, R. L.; Kornet, M. J.; Mahadevan, V.; Jerina, D. M. *J. Am. Chem. Soc.* **1964**, *86*, 5163.

(13) (a) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1424. (b) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766. (c) Bergbreiter, D. E.; Gray, H. N. *Chem. Commun.* **1993**, 645.

Table 1. Summary of the Synthesis and Characterization of the Copolymers of C_{60} with 4-Vinylbenzoic Acid (VBA)[a,b]

	components in polymn mixt					
entry	VBA (g)	C_{60} (mg)	AIBN (mg)	$M_n{}^c$	M_w	T_g (°C)
1	5		50	46 000	75 500	136
2	2.45	24.5	50			
3	2.50	125	50			
4	2.55	255	50			145
5	2.45	25	143			98
6	2.50	125	285			99

[a] Polymerization reactions were carried out at 70 °C as 10% solutions of the monomers in *o*-dichlorobenzene. [b] The compositions of these copolymers in the text represent the compositions of the initial polymerization mixtures. [c] GPC studies confirm high molecular weight copolymers (against polystyrene standard). Actual numbers are suspect in the light of microgel formation.

an argon atmosphere. We synthesized three copolymers containing varying amounts of C_{60} (1, 5, and 10 wt % with respect to VBA) in the reaction mixture. The polymerization mixtures were kept at this temperature for 24 h. While the monomer mixtures were soluble in the reaction media, the polymers precipitated out. After completion of the polymerization, the solvent was decanted and the brown colored residue was dissolved in methanol, filtered, and poured into excess diethyl ether. This process was repeated three times to obtain the desired C_{60}-containing VBA copolymers free from unreacted monomers. Interestingly, when treated with a 0.1 M aqueous NaOH solution, the polymers readily dissolved giving a light brown solution. Since C_{60} is insoluble in aqueous media, this also allows for complete removal of polymer unbound C_{60} molecules. Passing these alkaline polymer solutions through a filter paper followed by acidification of the filtrates with dilute HCl led to precipitation of the copolymers. The polymerization recipe and their physical properties are summarized in Table 1. GPC analysis provides molecular weights of the homo- and copolymers, and the presence of high polymer is confirmed. However, the actual numbers obtained for the molecular weight of the copolymers is suspect in light of the microgel formation. An increase in the level of incorporation of C_{60} in the copolymers is evident from the deepening in the color of the copolymer "solutions" (solvated microgel). While polyVBA is colorless, the copolymers produced light yellow to brown colored "solutions" with increasing fullerene content. The photographs of the methanol-solvated microgel of three different C_{60}–VBA copolymers containing varying amounts of C_{60} are shown in Figure 1. These methanol-solvated microgels are visually clear, and the increased C_{60} content in the copolymers is noted through darkening of the color.

We have utilized UV–vis, IR, and NMR spectroscopy to characterize and further establish the incorporation of C_{60} molecules in these copolymer chains. Figure 2 shows the IR spectra of polyVBA and the C_{60}–VBA copolymers obtained using 1 and 5 wt % of C_{60} in the polymerization mixture. The vibrational frequencies characteristic of polyVBA include 3481 cm^{-1} (OH), 1700 cm^{-1} (COOH), and 1610 cm^{-1} (aromatic C=C), while those due to C_{60} include 577, 1183, and 1429 cm^{-1}. Although the spectra of the homopolymer and copolymers look similar, a careful analysis provides some distinctions. While the peaks are well resolved in the
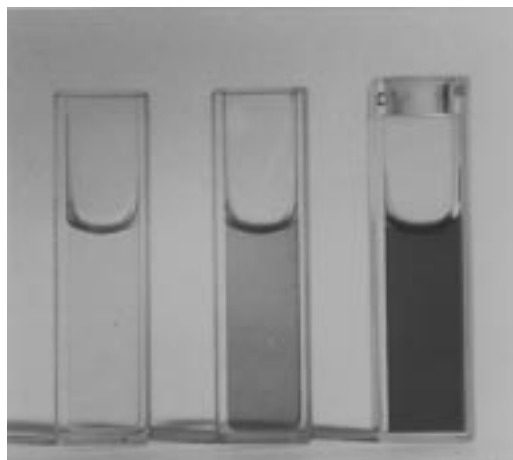
Figure 1. Photographs of methanolic solutions of VBA–C_{60} copolymers based on (a, left) 1 wt %, (b, center) 5 wt %, and (c, right) 10 wt % C_{60} in the polymerization mixture.
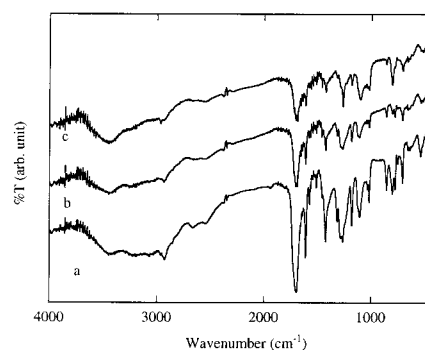
Figure 2. FT-IR spectra of (a) polyVBA and (b) VBA copolymer containing 1 wt % C_{60} and (c) VBA copolymer containing 5 wt % C_{60}.

case of polyVBA, they are, overall, broad for the copolymers. Interestingly, in the case of the copolymer obtained with 5 wt % C_{60} (Figure 2c), although a majority of the peaks have been broadened, the peak at 1425 cm^{-1} remains strikingly distinct. This characteristic peak which is due to the C_{60} moiety[14] appears to remain unaffected after being incorporated into the polymers.

Additional evidence supporting incorporation of fullerene units as a part of the polymer chains can be obtained from the UV spectroscopic analyses of these copolymers. The UV spectrum of pure C_{60} possesses two characteristic sharp absorption peaks near 330 and 260 nm.[16] The UV–vis spectra of these copolymers, on the other hand, are broad and featureless, tailing to the visible region. These features of the UV spectra are very similar to the earlier reported examples of copolymers of C_{60} with styrene and methyl methacrylate.[9] These earlier reports have ascribed such spectral features to changes in the symmetry properties of C_{60} nuclei upon substitution with polymer chains. Since in the case of C_{60}-containing polymers obtained either by

(14) (a) Kratschmer, W.; Lamb, J. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) Schlueter, J. A.; Seanman, J. M.; Taha, S.; Cohen, H.; Lykke, K. R.; Wang, H. H.; Williams, J. M. *Chem. Commun.* **1993**, 972.

(15) Beer, E.; Feuerer, M.; Knorr, A.; Mirlach, A.; Daub, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1087.

(16) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett.* **1991**, *177*, 394.
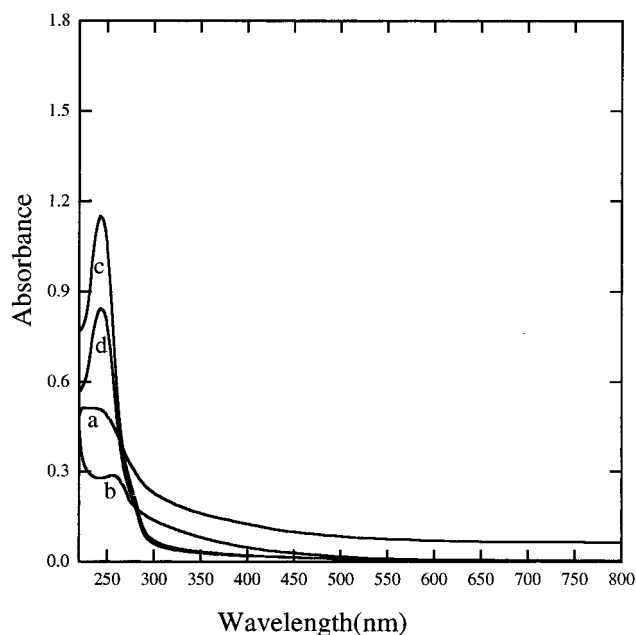
Figure 3. Electronic absorption spectra of (a) 5 wt % C_{60}–VBA copolymer in methanol, (b) copolymer after filtering through a 0.45 μm filter, (c) after filtering through a 0.2 μm filter, and (d) polyVBA.

Figure 4. Electronic absorption spectra of (a) C_{60} fullerene in dichloromethane (0.05 mg/mL) and (b) 5 wt % C_{60}–VBA copolymer cast film after being filtered through a 0.45 μm filter.

chemical modification[6] or polymerization of a C_{60}-functionalized monomer,[7] no change in the electronic spectra of C_{60} was observed, such an argument supporting changes in symmetry properties of C_{60} does not appear to be a valid proposition. As a matter of fact, a careful analysis by us revealed that the featureless spectra are a consequence of scattering rather than absorption.[17] This scattering of UV light arises from the formation of microgels during copolymerization of C_{60} with vinyl monomers (vide infra).

In general, intense scattering of electromagnetic radiation by polymer solutions is observed in the case of rigid rod polymers and microgels where the dimensions of the scatterer is larger than $\lambda/10$.[18] Being derived from common olefinic monomers, these polymer are less likely to be present as rigid rods. On the other hand, the presence of several reactive sites in C_{60} nucleus presents the possibility of incorporation of multiple polymer chains around it, leading to formation of cross-linked gels of micron dimension (microgels). While visually clear, these solvated microgels contain clusters that are of large enough dimension to strongly scatter the electromagnetic radiation in the UV region. To verify this possibility, we filtered the polymer samples through membranes of varying pore diameters (filter paper, 0.45 and 0.2 μm) and UV spectra of the filtrates were recorded. The UV spectra of the unfiltered copolymer based on 5 wt % C_{60} and that of the filtrates passing through 0.45 and 0.2 μm are presented in Figure 3. The spectra of the unfiltered sample and that filtered through 0.45 μm are similar, although the magnitude of the longer wavelength "absorbance" decreases with a decrease in the pore diameter of the filter
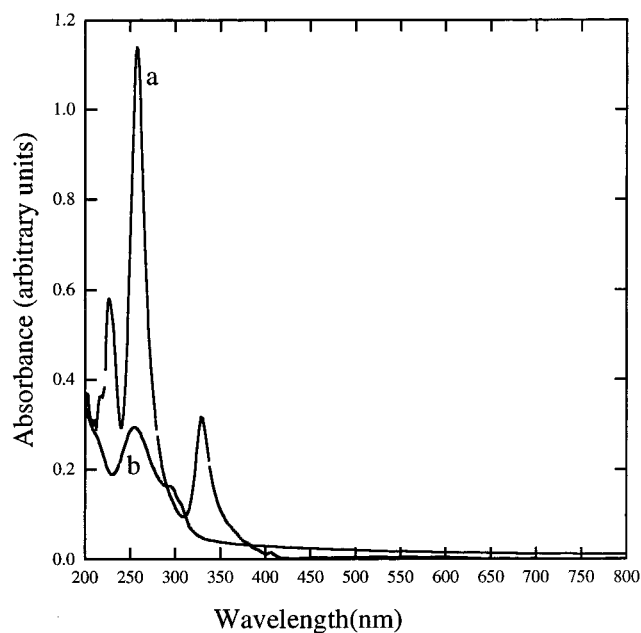
(Figures 3a and 3b). Interestingly, the spectrum of the filtrate passing through the 0.2 μm filter is completely devoid of the characteristic broad peak discussed above. This polymer shows a sharp peak at 250 nm (Figure 3c) which is identical to that of the polyVBA (Figure 3d). While the unfiltered polymers and the residue that did not pass 0.2 μm are brown colored, the residue obtained by evaporating this 0.2 μm filtered sample is clear and transparent. The similarity of its UV spectrum with polyVBA clearly suggests that this is the homopolymer of VBA. ^{13}C NMR analysis of this filtered sample shows no trace of C_{60} to be present in the polymer. The UV spectrum of the polymer sample filtered through 0.45 μm was also recorded in the form of a thin film cast from the filtered solution. Figure 4 represents the UV spectra of the C_{60} fullerene in dichloromethane (Figure 4a) and that of the 0.45 μm filtered sample of the copolymer as cast films (Figure 4b). This copolymer spectrum no longer structureless and is well resolved, showing the characteristic 260 nm peaks present in the pure fullerene. This result suggests that the electronic transitions associated with C_{60} nuclei are preserved in most cases with subtle variations upon incorporation of polymer chains. This suggests that results reported in earlier publications are conceivably due to scattering of UV light by polymer microgels, which seems to have been erroneously ascribed to UV absorption.[17]

Direct evidence of this scattering phenomenon exhibited by these copolymers can be visually observed by transmitting laser light of moderate intensity through these copolymers in methanol. A coherent beam laser light at 488 nm (blue Ar^+) was passed through a highly solvated sample (1 mg/mL) of polyVBA and C_{60}–VBA copolymer filtered through a filter paper. The state of the laser beam as it passes through these samples was captured photographically. While the laser beam passed through the homopolymer with very weak scattering, significantly stronger scattering (scattering streak) was

(17) Nayak, P. L.; Alva, S.; Yang, K.; Dhal, P. K.; Kumar, J.; Tripathy, S. K.; *Macromolecules* **1997**, *30*, 7351.

(18) (a) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958. (b) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Rowe: New York, 1971.

observed for the C_{60}−VBA copolymer (containing 5 wt % of C_{60}). This observation of scattering of laser beams from visually clear polymer solutions provides further supporting evidence for microgel formation during this copolymerization reaction.[17] Dynamic light scattering may be used to determine the size and shape of the scattering units quantitatively.[19]

Our careful study suggests that interpretation of the spectra and mechanism of fullerene−vinyl monomer copolymerization proposed appears to be erroneous. Since the UV spectrum of copolymer in the form of thin film shows the presence of the characteristic peaks of C_{60}, distortion of symmetry properties of C_{60} upon incorporation into a polymer chain leading to spectral broadening does not appear to be a valid proposition. In fact, the polymer chains are not true linear chains. Rather they are present as solvated clusters of micron to submicron size that are large enough to strongly scatter in the UV and short wavelength visible light yet small enough to appear as a clear solution in the visible light. Furthermore, the filtration experiment establishes the presence of some amount of the homopolymer (5−10 wt %, depending on the polymerization recipe) present in the copolymer sample that can only be separated through a rigorous filtration process. This is particularly important, since contamination of the copolymers with homopolymers would affect their thermomechanical as well as other physical properties.

Thus, carefully implemented filtration and spectral analysis studies suggest that free radical copolymerization of C_{60} with VBA produces polymers possessing microgel structures rather than true linear or branched chain macromolecules. Formation of these microgels can be rationalized on the basis of the following polymerization mechanism. The unique electronic structure of the fullerene nucleus containing 30 π bonds renders this molecule to possess strained, electron deficient polyene character. As a result, fullerene possesses the propensity to undergo ready polyaddition reactions with free radicals and nucleophiles. This behavior has been considered to be responsible for its participation in polymerization reactions with vinyl monomers. Thus, formation of the copolymers incorporating C_{60} units has been considered to commence by the reaction of C_{60} with growing polymer radicals. Among various possibilities by which the C_{60} can be incorporated in the polymer chain, the following two appear to be more reasonable (see Scheme 1). Reaction of the AIBN leads to formation of a C_{60} radical which becomes the site for chain growth by reacting with the monomer (path A). Another possibility may involve reaction of the growing polyVBA macroradical with C_{60} and subsequent chain propagation or termination (path B). The large molecular structure of C_{60} may make it sterically unfavorable to initiate a polymer chain by reacting with another molecule of C_{60} or VBA. This implies that C_{60} might act as a chain coupler with attachment of more than one growing polyVBA chain radical to a C_{60} moiety. From the above-mentioned UV study of the filtered samples, we propose that copolymerization of fullerene with vinyl monomers results in the formation of compact

Scheme 1

M = substituent of vinyl monomers
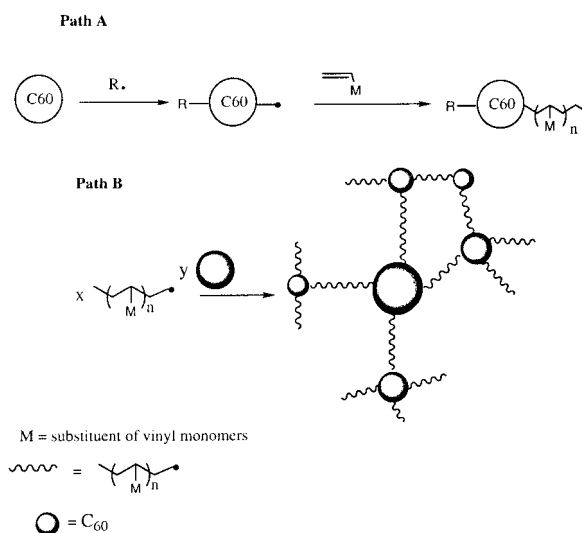
microgels with a C_{60} unit acting as a multifunctional monomer. This is plausible by considering the multifunctional nature of fullerene which has the propensity to undergo polyaddition with free radicals and nucleophiles.[8] In fact, during the process to prepare polymer pendant fullerene derivatives by nucleophilic addition of polyamines to fullerenes,[6a] gel formation was observed. This was ascribed to the polyvalent nature of fullerene. Thus, in these polymerization reactions, C_{60} is acting like a multifunctional vinylogous derivative resulting in lightly cross-linked polymer gels (steric restriction may not permit extensive cross-linking by reaction with all available sites).[20]

Fluorescence Properties. Novel optical properties exhibited by C_{60}-based functional materials have been the motivation to study the fluorescence properties of such materials.[21] The nature of C_{60} functionalization as a result of polyVBA segment attachments may also be further understood through their fluorescence spectra. We carried out variable wavelength fluorescence measurements on these VBA−C_{60} copolymers ranging from UV to visible excitation. Figures 5 and 6 show the fluorescence spectra of the polymers based on 5% and 10% C_{60}. Excitations were made at 290, 310, 330, and 350 nm. For this excitation range, certain features of the emission spectral patterns were found to be dependent on the wavelength of excitation for the 5% C_{60} copolymer and independent of the excitation wavelength for the 10% C_{60} copolymer. At excitation wavelengths of 290 nm, the emission spectra have a typical signature emission around 330 nm due to polyVBA.

The excitation wavelength-dependent fluorescence feature near 439 nm for the 5% C_{60} copolymer is ascribed to the possibility of inhomogeneous distribution of the emitting sites in the copolymers. Interestingly this feature has disappeared for 10 wt % C_{60} with the only emission feature occurring at 400 nm (Figure 6). This observation is unexplainable in the light of earlier

(19) Hugener, T. A.; Seery, T. A. P. Dynamic light Scattering of Water Soluble Polymers Containing Buckminsterfullerene, Proceedings of the 1997 MRS Fall Meeting.

(20) After this work was completed, Ford et al. reported the possibility of cluster formation during free radical copolymerization of C_{60} with vinyl monomers: Ford, W. T.; Graham, T. D.; Mourey, T. H. *Polym. Prepr.* **1997**, *38 (2),* 197.

(21) (a) Yang, L.; Dorsinville, R.; Alfano, R. *Chem. Phys. Lett.* **1994**, *26,* 605. (b) Kojima, Y.; Matsuoka, T.; Takahashi, H.; Kurauchi, T. *Macromolecules* **1995**, *28,* 8868.
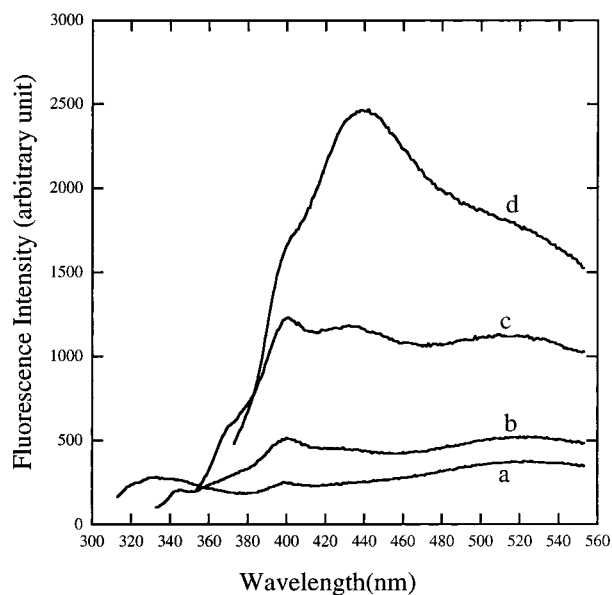
Figure 5. Fluorescence spectra of the 5 wt % copolymer of C$_{60}$ and VBA in methanol excited at (a) 290 nm, (b) 310 nm, (c) 330 nm, and (d) 350 nm.
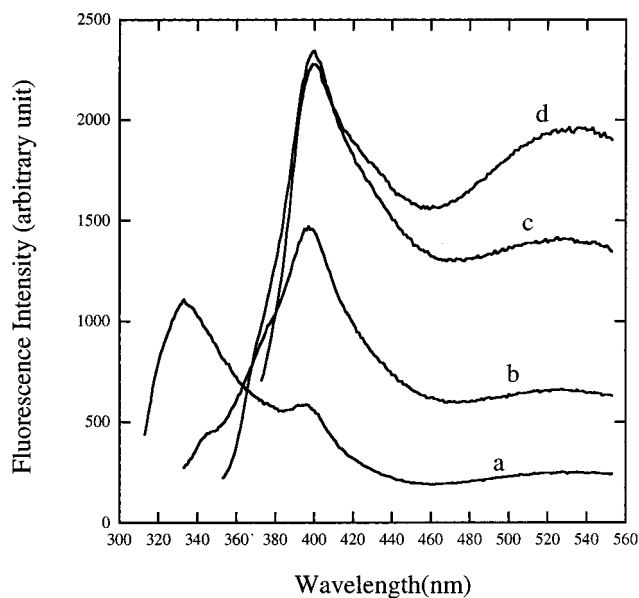

Figure 6. Fluorescence spectra of the 10 wt % copolymer of C$_{60}$ and VBA in methanol at (a) 290 nm, (b) 310 nm, (c) 330 nm, and (d) 350 nm.

claims that inhomogeneous distribution of the emitting sites in the copolymer might contribute to the wavelength-dependent fluorescence patterns of the copolymers. The copolymers containing varying amounts of C$_{60}$ should not possess very different structures in that case. Therefore, the formation of microgels especially at higher C$_{60}$ concentration (vide supra) appears to be playing an important role in the fluorescent behavior of these copolymers.

To ascertain this possibility, fluorescence measurements were carried out with unfiltered and 0.45 μm filtered samples. For 5% C$_{60}$ copolymer, emission spectra of the unfiltered and filtered samples (excited at 361 nm) are given in Figure 7. For the unfiltered sample (Figure 7a), the emission peak is very intense showing two peaks of comparable fluorescence yields near 408 and 427 nm. On the other hand, in the case
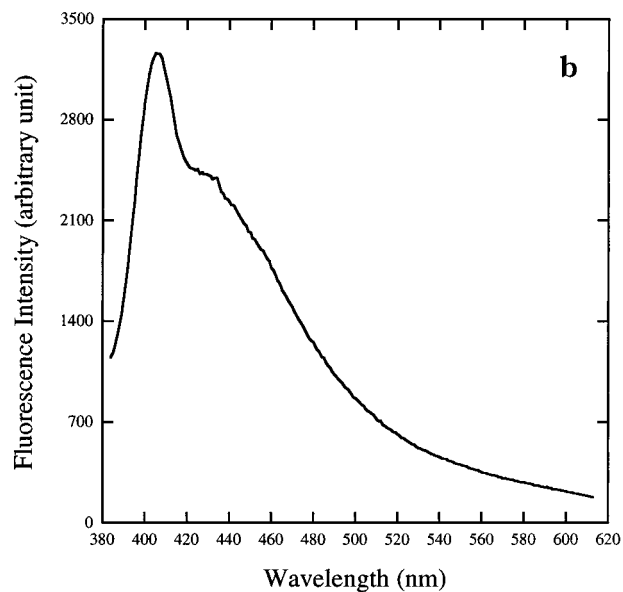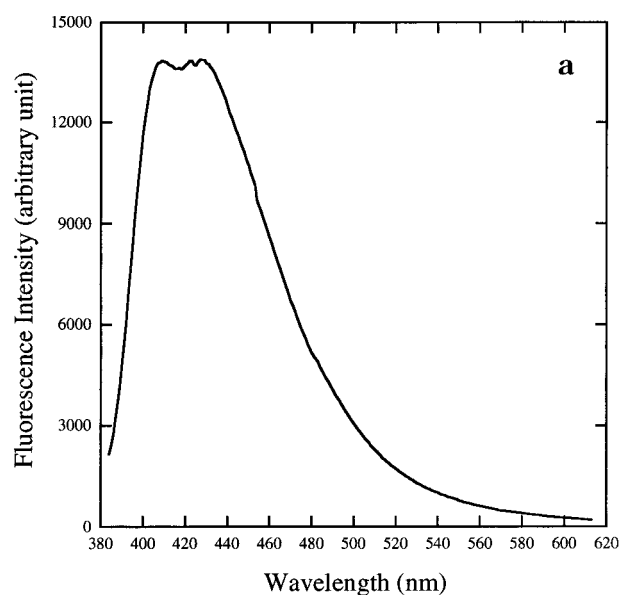

Figure 7. Fluorescence emission spectra of (a) unfiltered and (b) filtered samples of 5 wt % copolymer of C$_{60}$ and VBA at an excitation wavelength of 361 nm.

of the filtered sample (Figure 7b), the fluorescence yield of the 427 nm peak has decreased compared to the 408 nm peak. Similarly, the excitation spectra for the unfiltered and filtered samples of this copolymer are also different in intensity and pattern. While the unfiltered sample exhibits an intense narrow peak (Figure 8a), the filtered sample exhibits a less intense but broad and structured spectral pattern (Figure 8b). This observation further supports the heterogeneous structure of the copolymers and formation of microgels during copolymerization of C$_{60}$ with vinyl monomers. The microgels are not only of varying sizes, but their compositions appear to be different in this copolymer containing 5% C$_{60}$. Fluorescence emission spectra of the unfiltered and 0.45 μm filtered samples of the copolymer of VBA with 10% C$_{60}$ are given in Figure 9. The samples were excited at 289 nm, and the emission maximum was recorded at 336 nm. Although the fluorescence yield of the unfiltered sample (Figure 9a) is somewhat higher than that of the filtered sample (Figure 9b), the differ-
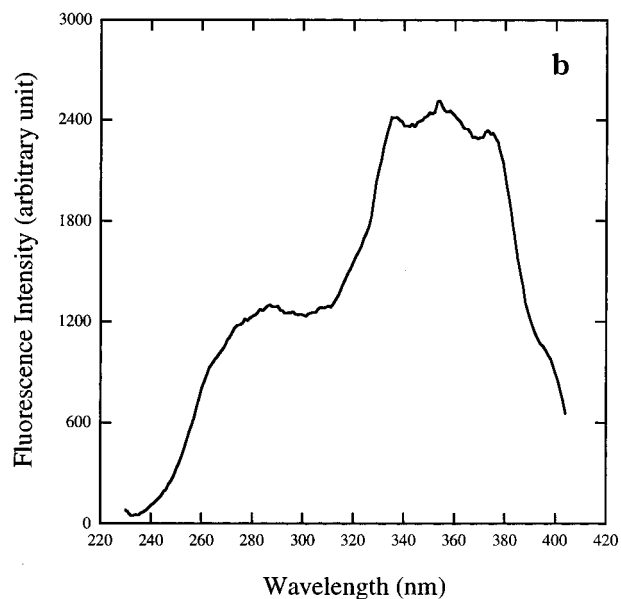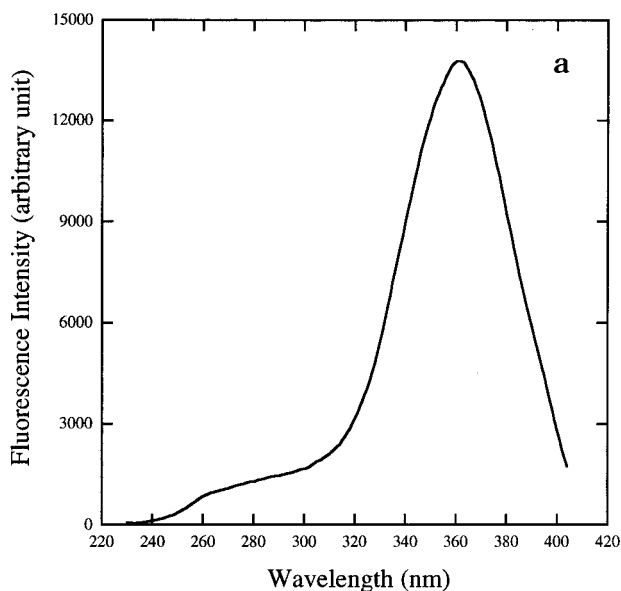
Figure 8. Excitation fluorescence spectra of (a) unfiltered and (b) filtered samples of 5 wt % copolymer of C_{60} and VBA observed at 427 nm.

Figure 9. Fluorescence emission spectra of (a) unfiltered and (b) filtered samples of 10 wt % copolymer of C_{60} and VBA at an excitation wavelength of 289 nm.

ence is not as significant as in the case of the 5% sample. It appears that with a higher concentration of C_{60} in the polymerization mixture, the microgels formed are of similarly functionalized moieties: they are homogeneous. A more careful study with copolymers synthesized with a wide range of vinyl monomer to C_{60} composition may aid in elucidating this fact.

Thermal Properties. Glass transition temperatures (T_g) and thermal degradation patterns of these C_{60}–VBA copolymers were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) methods. T_g of these polymers are presented in Table 1. T_g of the homopolymer of VBA was found to be 136 °C. T_g of the copolymer based on 10% C_{60} was found to be 145 °C (Table 1, entry 4). This suggests that C_{60} plays a nominal role on the T_g of the C_{60}-containing copolymers. In light of the complex structures of these copolymers, it is difficult to derive any meaningful conclusion from the T_g data.
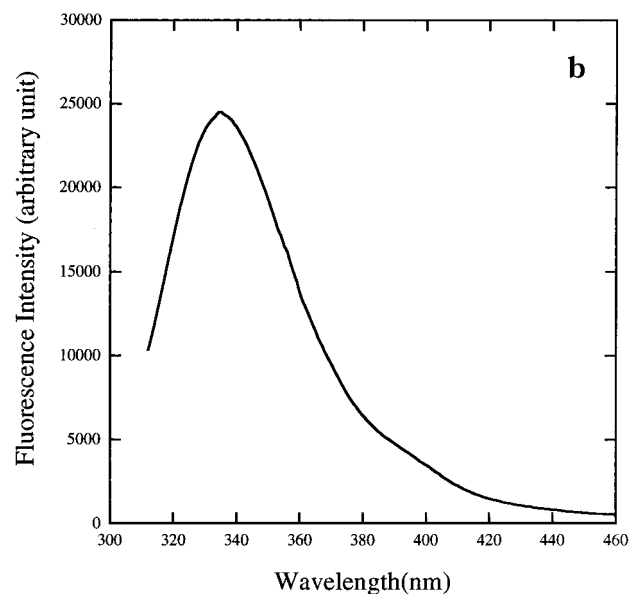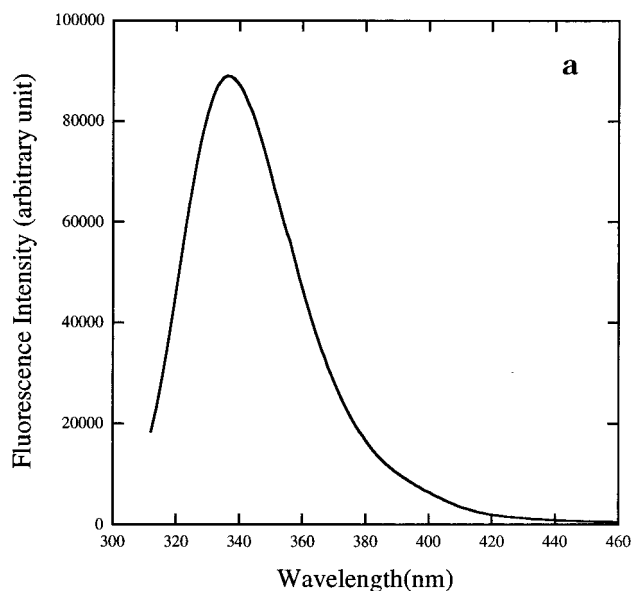
TGA thermograms of these polymers are shown in Figure 10. All the polymer samples exhibit multistage (2 or more) weight loss patterns. The low-temperature weight loss (~150 °C) may be due to the dehydration of the carboxylic acid units leading to formation of the corresponding polymeric anhydride structure. The subsequent weight losses can be ascribed to the degradation of the polymer backbones. Some interesting characteristics are exhibited in the thermal degradation pattern of these polymers. In general, the copolymers exhibited higher thermal stability than the homopolymer. Also, at 600 °C, the homopolymer has undergone complete degradation (Figure 10a), while the copolymers exhibit the presence of residual mass at this temperature. The copolymer based on 1 wt % C_{60} showed the highest initial thermal stability (Figure 10b), but subsequently it degraded at lower temperature. Similarly, copolymers based on 5% of C_{60} showed a lower thermal stability at the first stage weight loss, while it has higher stability for the second stage weight loss. On
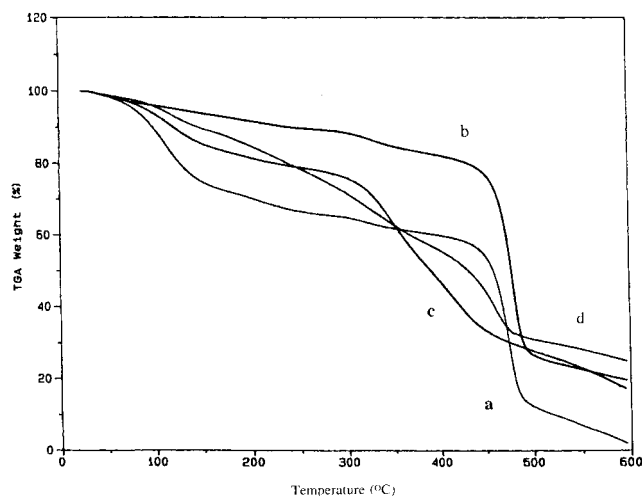
Figure 10. TGA thermogram of (a) polyVBA, (b) 1 wt %, (c) 5 wt %, and (d) 10 wt % of C_{60} and VBA copolymers.

the other hand, unpyrolyzed residue (char) content beyond 600 °C increased with increasing C_{60} content in the copolymer. This residual mass in the thermogram is the unpyrolyzed C_{60} residue that remains after complete degradation of the polymer. At this temperature C_{60} is thermally robust and has survived the pyrolysis. Increased residue content in the thermogram with increasing C_{60} in the polymer is expected in line with polymer composition. However, the nonlinear variation of the thermal stability of these copolymer as a function of C_{60} content in the polymers can be ascribed to the heterogeneous polymer structures involving microgel formation (vide supra). It is not unexpected to observe nonlinear thermal behavior when the copolymers besides possessing random structures are contaminated with homopolymer species. This obviously renders the composition−thermal stability correlation complicated.

Polyelectrolytic Behavior of the Polymer. These C_{60}-containing copolymeric microgels are highly solvated in methanol and are visually clear. While the polymers swell in water, upon addition of dilute NaOH to the aqueous dispersion, complete solvation of the polymers was observed. This behavior arises from the formation of polycarboxylate anions (polyelectrolyte). One of the typical polyelectrolyte characteristics of charged polymers in aqueous medium include increasing the specific viscosity with a decrease in concentration due to Coulumbic repulsion leading to chain expansion.[22] A plot of specific viscosity vs concentration of the copolymer based on 5 wt % C_{60} dissolved in dilute aqueous NaOH is shown in Figure 11a, which reveals this behavior. On the other hand, in the presence of 0.1 M sodium chloride, the specific viscosity decreases with dilution indicating that these polycarboxylates behave like neutral organic polymers (Figure 11b). This arises due to well-known charge screening behavior in the presence of excess small ion salts. Microgels must expand or contract as the polyelectrolyte chains tethered to the C_{60} contract and expand. Thus, an interesting new class of polyelectrolyte microgels containing fullerene moieties have been prepared.

(22) Hunkeler, D.; Wu, X. Y.; Hamielec, A. E. In *Polyelectrolyte Gels*; Harland, R. S., Prud'homme, R. K., Eds.; American Chemical Society: Washington, DC, 1992; ACS Symposium Series 480, p 53.
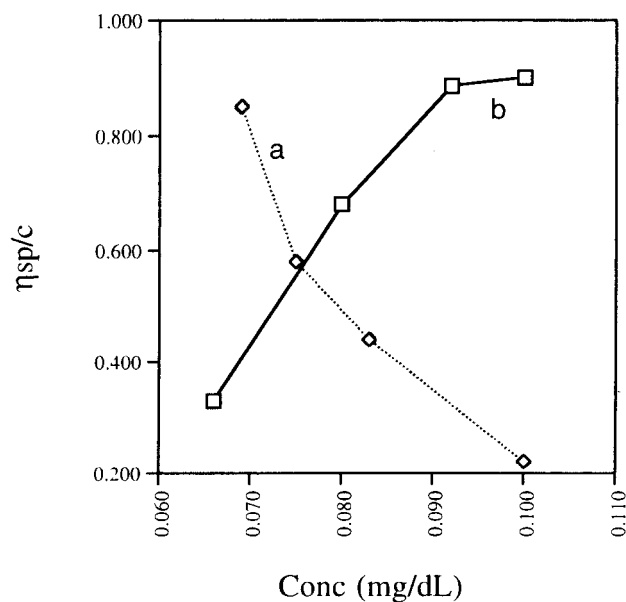

Figure 11. Plot of reduced specific viscosity (η_{sp}/c) vs concentration of (a) 5 wt % C_{60} VBA copolymer in dilute NaOH and (b) in the presence of a 0.1 M NaCl solution.

Langmuir−Blodgett (LB) Film. Interesting electronic and optical properties exhibited by fullerene-based materials make it desirable to prepare thin films based on such C_{60}-derived compounds. Among various techniques available for this purpose, the LB technique enables one to construct organic thin films that can be controlled at the molecular level.[23] Recently significant effort has been directed toward obtaining Langmuir films of C_{60} derivatives.[24] These studies include construction of LB films based on C_{60} involving floating layers on C_{60} at the air−water interface, from mixtures of C_{60} with other amphiphilic molecules as well as synthesis of amphiphilic derivatives with a variety of polar groups.[25] These methods resulted in thin films of varying success. Despite these reports, to our knowledge no effort has been made to prepare polymer-based C_{60} and their LB-forming properties. The polyionic nature of the polyVBA segments along with the hydrophobic characteristic of C_{60} should provide amphiphilic character to the copolymers. Furthermore, polymer-based LB films possess superior structural stability than their low molecular weight counterparts.[26]

Surface pressure−area isotherms for the homopolymer of VBA and the copolymers based on 5% and 10% C_{60} are shown in Figure 12. In all three cases, the monolayers exhibited a steep rise in surface pressure upon compression, suggesting formation of condensed phase. The monolayer of the homopolymer, however, does not show appreciable stability with a collapsed pressure of only 12 mN/m (Figure 12a). This is not

(23) Ulman, A., Ed. *Organic Thin Films and Surfaces: Directions for the Nineties*; Acadmic Press: New York, 1995.
(24) Costillo, R.; Ramos, S.; Ruiz-Garcia, J. *J. Phys. Chem.* **1996**, *100*, 15235.
(25) (a) Tomioka, Y.; Ishibashi, M.; Kajiyama, H.; Taniguchi, Y. *Langmuir* **1993**, *9*, 32. (b) Matsumoto, M.; Tachibana, H.; Azumi, R.; Tanaka, M.; Nakamura, T. *Langmuir* **1995**, *11*, 660. (c) Diederich, F.; Effing, J.; Jonas, U.; Jullien, L.; Plesnivy, T.; Ringsdorf, H.; Thilgen, C.; Weinstein, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *37*, 1599.
(26) (a) Lupo, D.; Prass, W.; Scheunemann, U. *Thin Solid Films* **1989**, *3*, 25. (b) Davis, E.; Hodge, P.; Towns, C. R.; Ali-Adib, Z. *Macromolecules* **1991**, *24*, 5695.
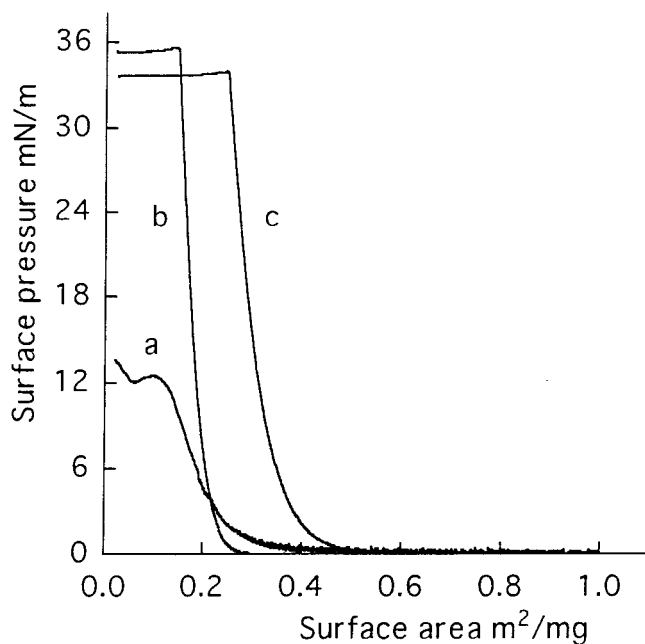
Figure 12. Surface pressure−area isotherms for (a) homopolymer of VBA, (b) 5 wt % C_{60} and VBA copolymer, and (c) 10 wt % copolymer C_{60} and VBA.

unexpected considering its rigid styrenic backbone bearing a polar carboxylic group without a lipophillic tail. On the other hand, both copolymers bearing C_{60} showed interesting properties. These copolymers possess a larger limiting area than the homopolymer and the polymer containing a higher amount of C_{60} possesses a larger limiting molecular area (Figure 12c). Furthermore, collapse pressure for monolayers of these copolymers is about 36 mN/m, significantly higher than that of the homopolymer. The covalent attachment of otherwise nonoptimal polymer chain such as polyVBA (to form Langmuir films) through fullerene units has resulted in a microstructure that enables production of molecularly stable thin films at the air−water interface. These monolayers are easily transferred by horizontal dipping processes to form multilayers.

In general, a combination of hydrophilic groups and long pendant alkyl chains is required for the formation of LB films based on polymers in order to provide optimal structural requirements to overcome the tendency to adopt a coiled conformation. However, rigid rodlike polymers such as polyglutamates and cellulosics have been found to form stable monolayers, which suggest that under conditions of sufficient natural chain extension a strong amphiphilic nature may not be required.[27] Furthermore, it has been recently reported that micrometer size polymer particles have been found to form monolayers at the air−water interface.[28] Thus, we reason that these hydrophilic polymers containing C_{60} connecting units have achieved a new type of structural form, enabling us to form the corresponding monolayers. These results are encouraging from the standpoint that it would enable one to produce molecularly thin layers of fullerene-containing polymer microgels with a homogeneous distribution of C_{60} moieties. Further studies are currently underway to prepare mono- and multilayers based on a variety of other functional copolymers containing C_{60} as well as their indepth characterization.

(27) (a) Wegner, G. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1326. (b) Schaub, M.; Fakirov, C.; Schmidt, A.; Lieser, G.; Wenz., G.; Wegner, G.; Albouy, P.-A.; Wu, H.; Foster, M. D.; Majrkzak, C.; Satija, S. *Macromolecules* **1995**, *28*, 1221.
(28) Du, H.; Bai, Y. B.; Hui, Z.; Li, L. S.; Chen, Y. M.; Tang, X. Y.; Li, T. J. *Langmuir* **1997**, *13,* 2538.