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Fullerene-End-Capped Polystyrenes. Monosubstituted Polymeric C_{60} Derivatives

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Polymeric fullerene derivatives are highly intriguing in view of the peculiar electrooptical properties of materials containing C_{60} homogeneously dispersed in a polymer matrix.[1] Polymer-bound C_{60} should be easily processable into thin films by spin-coating or casting. Covalent attachment of C_{60} to specific polymers may allow the combination of the electrooptical characteristics of fullerene with those of the polymeric matrix. Furthermore, polymer–fullerenes should also represent interesting model systems to study individual, isolated carbon clusters with respect to charge transport[2] and magnetic properties.[3] Drastic changes of the charge transport kinetics have been observed for fullerenes admixed to polymers.[4] However, little attention has been devoted to well-defined polymer–fullerenes[1,5–7] in comparison to the large number of reports on low molecular weight C_{60} derivatives,[8] since C_{60} has become available in larger quantities.[9]

The synthetic concepts described in the current literature are based on the reaction of functional polymers with C_{60}. For instance, amino-functional poly(imine)s have been reacted with C_{60} to form branched, soluble structures or networks,[5,15] which contain an extractable fraction of monosubstituted C_{60}. In a recent paper the synthesis of mainly monosubstituted polystyrene-C_{60} from azido-substituted polystyrene is described.[6] Samulski et al. have prepared multisubstituted polystyrene–fullerenes, which they designated "flagellanes".[7] Fréchet and co-workers have reported the synthesis of a dendrimer with a fullerene core.[10,18] Other approaches are based on the polycondensation of monomers[11,12] with attached C_{60}. However, no further data on the oligomeric or polymeric products have been reported.

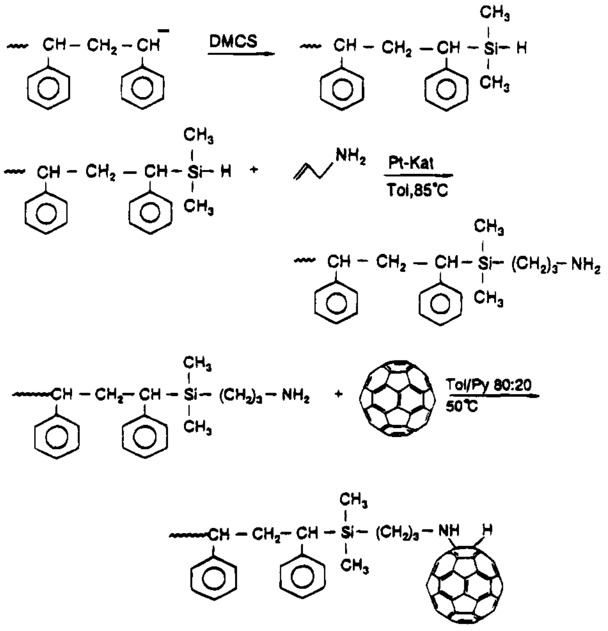
The preparation of fullerene derivatives is generally complicated by multiple substitution. In order to conbine the peculiar features of C_{60} with a polymeric matrix, it is desirable to retain the intact fullerene structure and related electrooptical properties, which are lost upon multiple reaction. However, the reaction of functional polymers with C_{60} commonly leads to large amounts of cross-linked, nonprocessable material due to multisubstitution, unless only small fractions of C_{60} are employed.[13–15] The preparation of soluble materials has been achieved in some cases.[5–7,10,18]

In this paper we give an account of the synthesis of C_{60}-end-capped polystyrene (PS-C_{60}) that can easily be processed to homogeneous and transparent films containing up to 27 wt % C_{60} by casting or spin-coating. The synthesis is based upon the reaction of amino-terminated polystyrene with C_{60}. An excess of C_{60} was employed to minimize the fraction of products with higher degrees of substitution. Fractionating precipitation enabled us to obtain exclusively monofunctional buckminsterfullerene–polystyrene, which was characterized by SEC equipped with UV and LALLS detectors.

Table 1. Amino-Terminated Polystyrenes and Fullerene–Polystyrenes

sample	M_w	M_n	NH_2 functionality (%)
PS-1	2 040	1 500	80
PS-2	14 500	11 800	90
PS-3	42 800	38 800	75

Scheme 1



In the first step, a series of amino-terminated polystyrenes (PS-NH_2) with relatively narrow molecular weight distributions was prepared by living anionic polymerization and subsequent end-capping by addition of dimethylchlorosilane (DMCS) and hydrosilation with allylamine. Three samples with M_w of 2040, 14 500, and 42 800, respectively, and amino functionality between 75% and 90% have been synthesized (Table 1).

Chemically, buckminsterfullerene is considered to behave like an electron-deficient olefin, reacting readily with nucleophiles, such as alcoholates or amines.[8] The reaction of PS-NH_2 with C_{60} was monitored in situ by following the UV absorption band between 415 and 430 nm, which is characteristic for monosubstitution of C_{60}.[5] A fiber optics probe was used directly in the reaction mixture for this purpose. In model studies with dodecylamine we observed that the use of pyridine as a polar cosolvent shortens the reaction time considerably. Pyridine is inert toward C_{60}. Therefore, in all reactions of C_{60} with amino-functional polystyrene, a mixture of 80/20 toluene/pyridine was employed. This resulted in reaction times between 4 and 6 days, which were considerably shorter than those observed in pure toluene. The general synthetic route is shown in Scheme 1.

In all reactions a ratio of 2:1 C_{60}/polystyrene was used to minimize the fraction of higher substituted products. Excess fullerene was separated by dissolving the products in THF to remove unreacted C_{60}, which was recycled. Monosubstituted C_{60} derivatives exhibit characteristic UV bands,[5] which, in contrast to pure C_{60} and derivatives with higher degrees of substitution, show a narrow absorption band between 415 and 435 nm as well as a broad band centered at 530 nm. Parts a–c of Figure 1 depict the UV spectra of pure C_{60} and the reaction mixture PS-NH_2/C_{60} after various reaction

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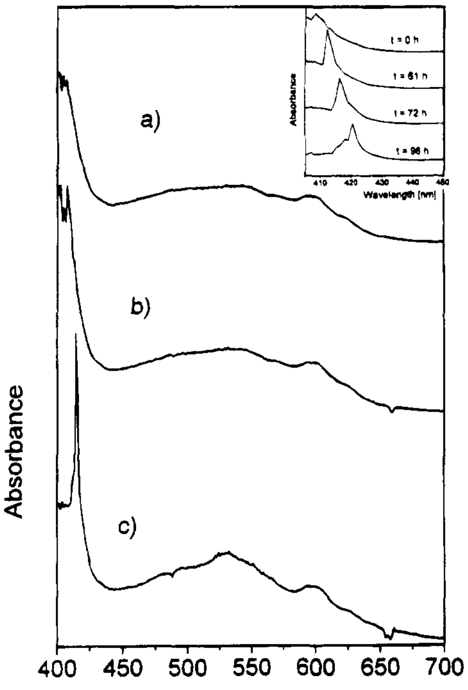

Figure 1. UV spectra of the reaction of PS-3 with C_{60} measured after various reaction times; (a) 61, (b) 72, and (c) 96 h. Spectra demonstrate the formation of a narrow absorption band at 423 nm. The inset shows the bathochromic shift in the course of the reaction.

times (sample PS-3, $M_w = 42\ 800$). Initially, an absorption between 405 and 410 nm was observed. In the course of the reaction this absorption transformed into a narrow band, that underwent a bathochromic shift to its final position between 420 and 423 nm. This was observed in the same manner for all three PS samples regardless of molecular weight. The bathochromic shift of the narrow absorption band from 409 to 423 nm in the course of the reaction is shown in the inset of Figure 1 and has not been described before. Surprisingly, a comparison of samples taken after 72 and 144 h of reaction time by SEC revealed that C_{60} is already attached to polystyrene after 72 h, i.e., before the bathochromic shift of the absorption band to its final position occurs. Therefore, we tentatively attribute the shift of the UV absorption subsequent to the reaction with PS-NH_2 to a rearrangement of C_{60} to the thermodynamically most stable isomer, as is also known for other substitution reactions of C_{60}.[16,19] A more precise investigation of this phenomenon is in progress.[17]

The crude mixture of polymer–fullerenes was fractionated carefully after the reaction for PS-2 and PS-3. This was accomplished by slow addition of isopropyl alcohol to a toluene solution of the polymers. In order to compare molecular weights and determine the fraction of monosubstituted and higher substituted PS-C_{60}, SEC equipped with UV and LALLS (low-angle LASER light scattering) detectors was used. The detection wavelength of the UV detector was set to 300 nm, which is specific for C_{60}.

SEC (Figure 2) evidences that fractionation leads to monosubstituted PS-C_{60}. Parts a and b of Figure 2 show the SEC diagrams for the amino-terminated PS-3 ($M_w = 42\ 800$) at detector wavelengths of 300 and 254 nm, respectively. Polystyrene can only be detected at 254 nm. After the reaction the product mixture of monosubstitued PS-C_{60} and fractions of higher substituted $(PS)_n$-C_{60} derivatives (Figure 2c) could be fractionated to obtain monosubstituted fullerene–polystyrene, which was obtained in >96% purity with traces of the disubstituted product (Figure 2d). Similarly, in the case of PS-2 ($M_w = 14\ 500$), the monosubstituted PS-C_{60} was obtained after repeated precipitation. The fractionation was more difficult in the case of PS-1, where the monosubstituted fullerene could not be separated cleanly from products with higher degrees of substitution by precipitation. The crude yields of C_{60}-substituted polystyrenes ranged between 85 and 90%, for PS-1, PS-2, and PS-3, respectively. The final yield of monosubstituted PS-C_{60} after fractionation was 55% (PS-3) and 30% (PS-2). Due to the amino functionality of PS-NH_2 (PS-3), PS-C_{60} still contained 25% of inseparable, nonfunctional polystyrene.

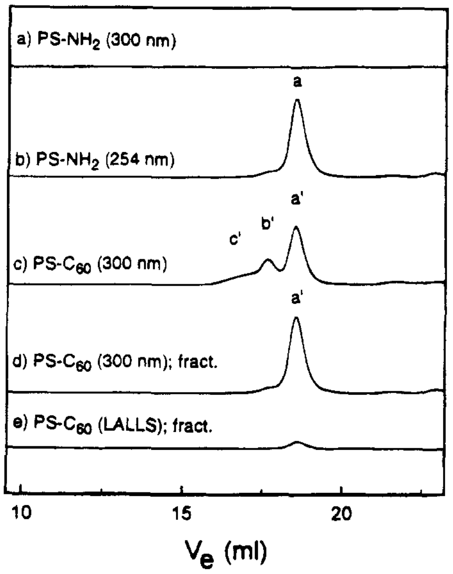

Figure 2. SEC of PS-NH_2 with the UV detector at 300 nm (a) and the detector at 254 nm (b), the product mixture after the reaction (c), and the final product PS-C_{60} (d and e). The respective molecular weights (M_w) (SEC, PS standards) are (a) 42 800, (a') 42 900; (b') 79 900, and (c') 214 000.

Table 2. End-Capped Polystyrene-C_{60} Samples after Fractionation

sample	M_w	M_n	λ_{max} (nm)
PS-2-C_{60}	15 000	12 100	420
PS-3-C_{60}	42 900	38 900	423

All polystyrene–fullerenes were obtained as brown, brittle glasses. The intensity of the brown color depended on the amount of fullerene incorporated and was most intense for PS-01 ($M_w = 2040$). The glass transition temperatures ranged between 65 (PS-1) and 91 °C (PS-3) and remained thus unchanged in comparison to the nonfunctional polystyrenes, in contrast to recent results obtained on polystyrenes with C_{60} side groups.[6] Molecular weights as well as the wavelength of the narrow absorption band are summarized in Table 2 for the fractionated samples.

Figure 3 shows the ^{13}C-NMR spectrum of PS-C_{60} for PS-1 ($M_w = 2040$). All resonances were assigned unambiguously. The spectrum confirms that C_{60} is covalently attached to the polystyrene chain. The inset depicts the C_{60} resonances as well as the ipso-carbon of the phenyl group. The end groups are also clearly discernible.

Figure 4 illustrates the different morphologies of blends of PS-NH_2/C_{60} in comparison to all fullerene-end-

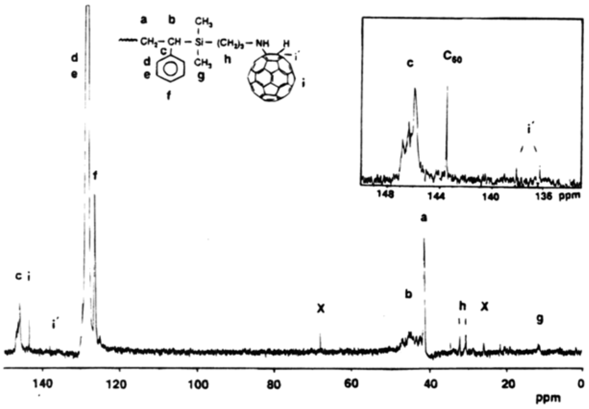

Figure 3. ^{13}C-NMR spectrum of PS-C_{60} (PS-1). Inset: spectral region of C_{60} resonances enhanced.

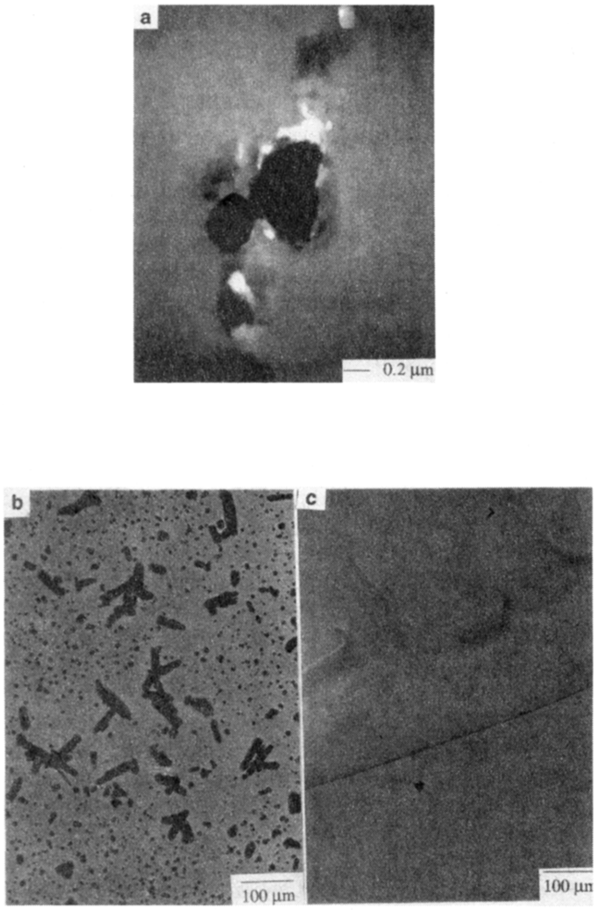

Figure 4. (a) TEM image of a blend of PS/C_{60} prepared by coprecipitation from solution. (b) C_{60} melt blended with PS (light microscopy). (c) Transparent film of C_{60}-end-capped polystyrene (PS-C_{60}) (light microscopy).

capped polystyrene samples (PS-C_{60}). Fullerene was immiscible with polystyrene in solution as well as in the melt. Coprecipitation of C_{60} and polystyrene (MeOH) led to crystallization of C_{60} in the PS matrix (Figure 4a, TEM image). The formation of larger crystals to C_{60} occurred upon blending C_{60} with PS in the melt (Figure 4b, light microscopy). In contrast to these observations, transparent and homogeneous films were obtained for all polystyrene–fullerenes studied. Light microscopy revealed homogeneity on a micron scale (Figure 4c). The homogeneous character of the films was confirmed by electron microscopy, which showed a uniform morphology indistinguishable from pure polystyrene for all samples. Thus, even at length scales of 10 nm no phase separation due to crystallization could be detected. This was also supported by investigation of the surfaces of thin films of PS-C_{60} by scanning force microscopy, which did not reveal any phase separation. The homogeneous morphology is in agreement with results on C_{60}-containing polystyrene copolymers reported recently.[6]

Conclusion. Well-defined fullerene-end-capped polystyrenes were prepared by reaction of amino-terminated polystyrene with C_{60} and subsequent fractionation. The polymers formed clear and homogeneous films, i.e., no micro- or nanophase separation was observed, as is common for blends of C_{60} with polystyrene. In contrast to the observations of Samulski et al., no lamellar morphology was observed. The fullerene-terminated polymers are intriguing from a chemical point of view, e.g., for the preparation of well-defined stars based on C_{60}. At present, a further study of the electrooptical properties of the materials is in progress. First measurements revealed a considerable increase of the conductivity of the C_{60}-end-capped polystyrenes in comparison to pure polystyrene.

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References and Notes

(1) Hirsch, A. *Adv. Mater.* **1993**, *5*, 859.
(2) Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127.
(3) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.
(4) Wang, Y.; West, R.; Yuan, Ch. *J. Am. Chem. Soc.* **1993**, *115*, 3844.
(5) Geckeler, K. E.; Hirsch, A. *J. Am. Chem. Soc.* **1993**, *115*, 3850.
(6) Hawker, C. J. *Macromolecules* **1994**, *27*, 4836.
(7) Samulski, E. T.; DeSimone, J. M.; Hunt, M. G., Jr.; Mencelogu, Y. Z.; Jarhagin, R. C.; York, G. A.; Labat, K. B.; Wang, H. *Chem. Mater.* **1992**, *14*, 9665.
(8) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.
(9) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.
(10) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J.; Wudl, F.; Srdanov, S.; Shi, S.; Li, C.; Kao, M. *J. Am. Chem. Soc.* **1993**, *115*, 9836.
(11) Wang, J.; Javahery, G.; Petrie, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9665.
(12) Wang, J.; Javahery, G.; Petrie, S.; Hopkinson, A. C.; Bohme, D. K. *J. Am. Chem. Soc.* **1994**, *106*, 227.
(13) Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977.
(14) Olah, G. A.; Bucsi, I.; Lambert, C.; Anisfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9387.
(15) Patil, A. O.; Schriver, G. W.; Carstensen, B.; Lundberg, R. D. *Polym. Bull.* **1993**, *30*, 187.
(16) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231.
(17) Weis, C.; Mülhaupt, R.; Frey, H., manuscript in preparation.
(18) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 925.
(19) Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem.* **1991**, *103, 10*, 1339.

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