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Synthesis of fullerene- and fullerol-containing polymers

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Fullerenes have been covalently attached along polydiene chains *via* a lithiation reaction. Ultraviolet–visible (UV–VIS), Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) measurements, together with thermal gravimetric analyses (TGA), indicate that both highly soluble and crosslinked polymeric fullerene derivatives can be prepared under appropriate reaction conditions. Furthermore, an aqueous methanol solution of hydrochloric acid is shown to be an efficient reagent for the conversion of the polymer-bound fullerenes to fullerols.

Introduction

Fullerenes have attracted a great deal of interest since the discovery that [60]fullerene, C_{60}, has a soccer-ball like structure—a truncated icosahedron.[1] Fullerenes and their derivatives have been shown to possess unusual photonic, electronic, superconducting and magnetic properties.[2] The large-scale synthesis of fullerenes[3] has made C_{60} readily available and chemical modification of fullerenes has since attracted considerable attention.[4–14] In particular, the combination of the unique molecular characteristics of fullerenes with good processability of certain polymers through chemical modification has proved promising for making advanced polymeric materials with novel physicochemical properties. In this regard, fullerenes have been chemically bonded onto some tractable polymer chains either as pendant groups or as constituent units of the polymer backbones. For instance, the chemical or photo-polymerization of C_{60} has been demonstrated to produce polymer backbones containing C_{60} entities,[15] while the amine addition of amino-polymers into fullerene double bonds[16] and the cycloaddition reaction of functionalized polymers with C_{60}[17,18] have been shown to generate fullerene-grafted polymer chains.

We have recently demonstrated that C_{60} can also be covalently attached onto 1,4-polydiene chains, such as 1,4-polybutadiene and 1,4-polyisoprene, through lithiation of the polymer chains with *sec*-butyllithium (Bu^sLi), followed by chemically bonding fullerenes onto the lithiated polymer chains and quenching with MeOH. Preliminary results, previously reported in a short communication,[19] have shown that the resulting C_{60}-functionalized polydiene materials with multiple pendant fullerenes dispersed along their polymer backbones are highly soluble and thermally processable, which could open up novel applications for fullerenes. In our further investigation on fullerene-containing polymers, we found that C_{60}-crosslinked polydiene elastomers can also be prepared *via* the lithiation reaction under certain reaction conditions. Furthermore, an aqueous methanol solution of hydrochloric acid was shown, for the first time, to be an efficient reagent for the conversion of the polymer-bound fullerenes to fullerols. In this paper, we present these new findings, together with the details of syntheses and spectroscopic characterization of the fullerene- and fullerol-containing polymers.

Experimental

Materials

While *cis*-1,4-polybutadiene (98% *cis*, $M_w = 2\,500\,000$) was purchased from Aldrich, the *cis*-1,4-polyisoprene was anionically synthesised in cyclohexane at room temp. (20 °C) using *n*-butyllithium as the initiator. The synthesis and characterization of the *cis*-1,4-polyisoprene have been previously reported in detail elsewhere.[20–23] The fullerene sample was purchased from Aldrich, as were the analytical grade tetramethylethylenediamine (TMEDA), Bu^sLi (supplied in cyclohexane), cyclohexane and methanol. Hydrochloric acid in water (36 mass%) was used as supplied by Ajax Chemicals.

Synthesis

In a typical experiment, we carried out the grafting reaction shown in Scheme 1 (reactions 1–3) by dissolving 100 mg of *cis*-1,4-polyisoprene or *cis*-1,4-polybutadiene in 10 ml of dry cyclohexane (or benzene) under an argon atmosphere at room temp. Then, a predetermined amount of Bu^sLi was added with stirring,[24] and to the stirred solution TMEDA was subsequently injected at a 1 : 1 molar ratio with respect to Bu^sLi (TMEDA was used to enhance the efficiency of the metallation of diene polymers[19]). The colour of the reaction mixture changed from pale-yellow to dark-red in a few minutes, as the reaction progressed. The reaction mixture was further stirred at room temp. for about 2 h before a selected amount of C_{60} (pre-dissolved in toluene or benzene) was added at a fixed molar ratio of Bu^sLi to C_{60}, depending on whether a soluble or a crosslinked form of the final product was desired.[24] Consequently, a colour change from dark-red to dark-brown was observed. Thereafter, the fullerene-functionalized polymeric adduct was quenched and precipitated by addition of methanol. The soluble C_{60}-grafted polymer was then redissolved into THF and this was followed by centrifugation to remove unreacted C_{60} (if any), as the solubility of free fullerenes in THF is negligibly low.[25] The soluble C_{60}-grafted polymer was finally separated into THF as a brass-coloured solution. In cases where C_{60}-crosslinked polymer gels were produced, any unreacted C_{60} and uncrosslinked polymer chains were removed by thoroughly washing with pure benzene.

Fullerol-containing polydienes were prepared in two different ways. Method 1: during the synthesis of the C_{60}-containing polydienes, the lithiated C_{60}-containing intermediate (*i.e.* Product **III** of Scheme 1) was terminated by an undegassed aqueous HCl (36 mass%)–methanol solution (1 : 1 v/v) instead

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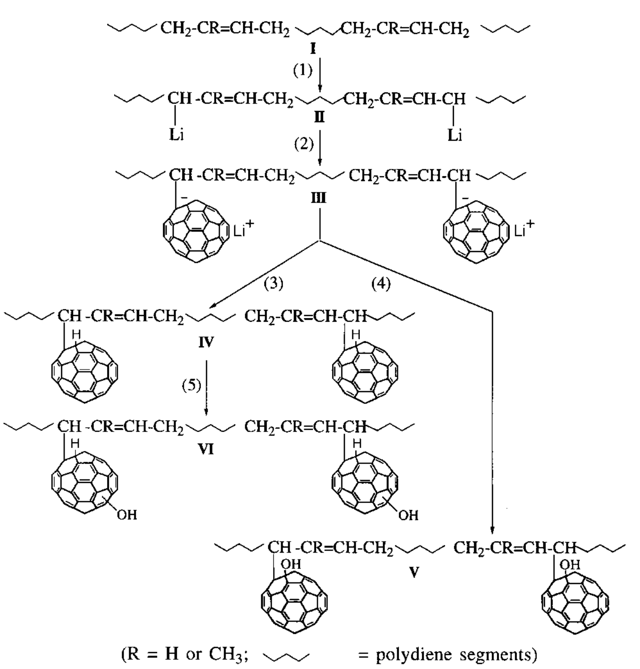
† Currently renamed as: CSIRO Molecular Science.



Scheme 1 Lithiation of polydienes followed by reaction with fullerene and its subsequent conversion to fullerols (The exact position and number of the hydroxy group(s) in Product **VI** are yet to be determined). *Reagents and conditions*: (1) Bu^{s}Li, TMEDA; (2) C_{60}; (3) MeOH; (4) HCl, H_2O, MeOH (O_2); (5) HCl, H_2O, MeOH (O_2).

of methanol alone (reaction 4 of Scheme 1). Method 2: the purified C_{60}-grafted polymers (*i.e.* Product **IV** of Scheme 1) were treated with the undegassed aqueous HCl–MeOH solution at room temp. (reaction 5 of Scheme 1).

Characterization

The ultraviolet–visible (UV–VIS) spectroscopic measurements were carried out using a Hewlett-Packard HP-8451A spectrometer. FTIR spectra were measured on polymer samples cast on a KRS-5 crystal, using a Mattson Alpha Centauri FTIR spectrometer with a resolution of 4 cm^{-1}. Solution NMR measurements were performed on a Bruker AC-200 NMR spectrometer using deuterated chloroform (99.8% D) as solvent. High-resolution solid state ^{13}C NMR spectra of dried samples were collected on a Varian Unity Inova-300 spectrometer at resonance frequency 75.4 MHz under conditions of magic angle sample spinning (MAS) and high-power dipolar decoupling (DD) by using either a single 90° pulse sequence with a repetition time of 2 s or the cross-polarization (CP) pulse sequence at a contact time of 2 ms and a repetition time of 3 s. The 90° pulse-width was of 3.7 μs while the rate of MAS was 9–10 kHz. The chemical shift of ^{13}C spectra was determined by taking the carbonyl carbon of solid glycine (176.03 ppm relative to $SiMe_4$) as an external reference standard. Gel permeation chromatographic (GPC) measurements were made on a Waters Associates GPC unit using tetrahydrofuran (THF) as solvent and a polystyrene standard. All the spectroscopic measurements were made at room temp. unless otherwise stated. Thermal analyses were made using a thermal gravimetric analyser (TGA, Mettler TG50).

Results and Discussion

Soluble fullerene-containing polymers

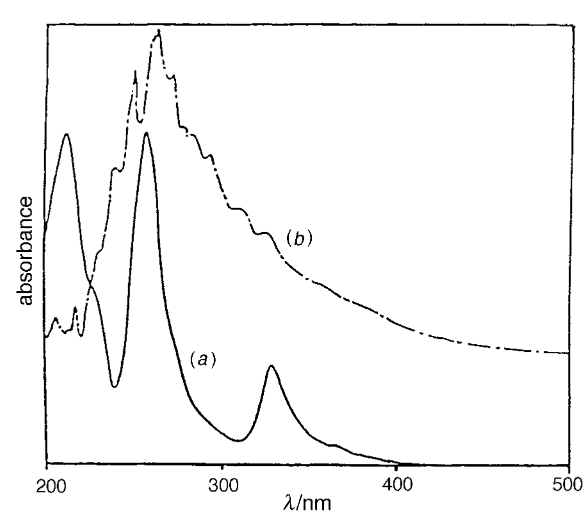


Fig. 1 UV–VIS absorption spectra of (*a*) C_{60} in cyclohexane; (*b*) the purified MeOH-terminated C_{60}-grafted polybutadiene diluted in THF

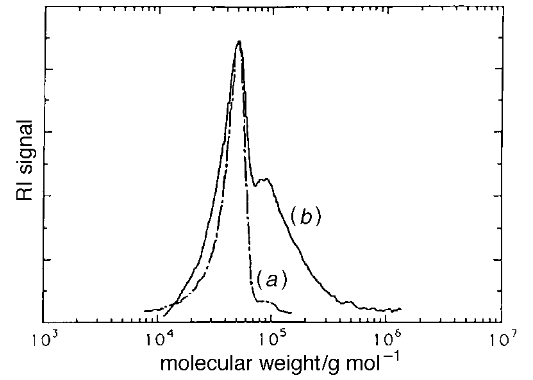


Fig. 2 GPC chromatograms of (*a*) the pristine *cis*-1,4-polyisoprene in THF recorded by the refractive index detector; (*b*) C_{60}-grafted polyisoprene in THF recorded by the refractive index detector

Soluble fullerene-functionalized polydiene chains were prepared according to the reactions shown in Scheme 1 (reactions 1–3) at low molar ratios of Bu^{s}Li to C_{60} (*i.e.* [Bu^{s}Li]/[C_{60}]<1).[24] The lithiation reaction was reflected by a color change from colorless, through pale-yellow, to dark-red, and a continuous red-shift in the UV–VIS spectrum. The UV–VIS spectra of pure C_{60} and the resulting brass-coloured solution of C_{60}-grafted polydienes diluted in THF are shown in Fig. 1(*a*) and (*b*), respectively. Comparison of curve (*b*) with curve (*a*) shows the appearance of several new absorption bands. This is accompanied by the disappearance of the characteristic peaks of fullerene at 213 and 329 nm,[26] suggesting the formation of polymeric fullerene derivatives. A similar decrease in the absorption at 329 nm observed for calixfullerene was attributed to the isolation of C_{60} by the intramolecularly linked calix[8]arene,[27] while the appearance of peaks at 213, 248, 257, 308 and 326 nm had been taken as evidence for mono-addition of fullerenes in other cases.[6,16,28] The expected absorption characteristic of the fullerene mono-adduct in the region 415–435 nm[16,29] was very weak, with respect to those peaks in the UV region, and became apparent only after scaling up the axis of absorbance as was the case for C_{60}-capped vinyl ether oligomers.[29] The other newly appeared weak absorption bands seen in Fig. 1(*b*), however, may indicate the occurrence of slightly higher degrees of addition onto traces of C_{60}.

The grafting reaction shown in Scheme 1 (reactions 1–3) was also followed by GPC measurements. The GPC chromatograms for the pristine polyisoprene [curve (*a*)] and a purified C_{60}-grafted polyisoprene [curve (*b*)] recorded with a refractive index (RI) detector are shown in Fig. 2. As can be seen in Fig. 2(*a*), the anionically polymerized polyisoprene has a very narrow molecular mass distribution ($M_w/M_n = 1.1$) with a weight-average molar mass (polystyrene equivalent) $M_w = 44\,000$ g mol^{-1}. Fig. 2(*b*), however, shows the appearance of a shoulder at higher molecular mass while the peak corresponding to that of Fig. 2(*a*) remained unshifted. As a result, new values of $M_w = 95\,000$ g mol^{-1} and $M_w/M_n = 1.8$ were obtained for the modified polymer. A similar change in GPC chromatograms has previously been observed for the cycloaddition of C_{60} onto azido-substituted polystyrenes with mono-addition being the dominant process.[17] Thus, the reasonably small value of the polydispersity (*i.e.* $M_w/M_n = 1.8$) for the C_{60}-grafted polyisoprene suggests that cross-linking, if any, was insignificant at the low ratio of $[Bu^sLi]/[C_{60}]$ although gel formation was observed for the grafting reactions carried out at high degrees of lithiation and a low molar ratio of C_{60}, as we shall see later. The corresponding GPC result measured by a UV–VIS detector at $\lambda = 326$ nm, a wavelength at which only the fullerene absorbs,[21,22,26] confirms that the higher molecular mass species associated with the shoulder in Fig. 2(*b*) correspond to the fullerene-grafted polyisoprene chains, as only the species of higher molar masses were observed by the UV–VIS detector. As a control, GPC measurements were also made on the lithiated, fullerene-free polyisoprene, after it had been quenched by MeOH in the same manner as for the fullerene-grafted polyisoprene. No change in the molecular mass with respect to the polyisoprene precursor was found. Therefore, the differences between curves (*a*) and (*b*) in Fig. 2 can be attributed to the grafting reaction of C_{60} onto the polymer chains.

The presence of the peak corresponding to the *cis*-1,4-polyisoprene precursor in Fig. 2(*b*), however, indicates that a significant amount of the polyisoprene chains did not react with C_{60} in this particular case, presumably due to a low efficiency of lithiation and/or the aggregation of polyisoprenyllithium chains[30] which could physically trap some of the ‘living’ lithium sites away from the grafting reaction. It is also worth pointing out that GPC measures the hydrodynamic volume of a macromolecular chain rather than its absolute molar mass. From the GPC results, therefore, a calculation of the molar percentage of C_{60} in the host polymeric chains cannot be made without detailed information on changes in the polymer conformation upon the grafting reaction.[10] Nevertheless, the percentage incorporation of C_{60} into the polydiene chains can be estimated from the thermal gravimetric analyses (see below).[17]

The purified C_{60}-grafted polydiene chains (Product **IV** of Scheme 1) were analysed by FTIR measurements. As shown in Fig. 3(*a*), the band at 715 cm^{-1} is characteristic of the $=$CH out of plane (bending) deformation of the pristine polybutadiene, while the band at 1670 cm^{-1} corresponds to the stretching vibration of the isolated C$=$C bonds.[31–33] The deformation and stretching vibration of $-CH_2-$/$-CH-$ bonds in the pristine polybutadiene chains are observed at 1445 cm^{-1} and 2700–3000 cm^{-1}, respectively.[31–33] For the C_{60}-grafted polybutadiene after being terminated by pure MeOH [Fig. 3(*b*)], the absorption band characteristic of $-CH_2-$ deformation vibration at 1445 cm^{-1} changed shape considerably. This was accompanied by the appearance of several broad absorption peaks centered at 1470, 1140 and 500 cm^{-1} which are assigned to [60]fullerene, with the expected peaks[26,34] at 1428, 1181, 578 and 528 cm^{-1} shifted somewhat as a result of chemical interactions with the polymer backbone. However, almost no detectable change was observed for the characteristic absorption bands of the C$=$C bonds at 715 and 1670 cm^{-1}. These spectroscopic changes confirm the occurrence of the intended coupling reaction (Scheme 1) with C_{60} being attached onto saturated aliphatic carbons along the polydiene chains.

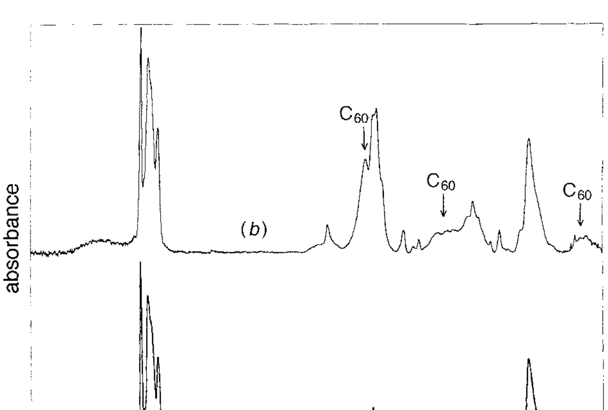


Fig. 3 FTIR spectra of (*a*) the pristine *cis*-1,4-polybutadiene; (*b*) C_{60}-grafted *cis*-1,4-polybutadiene terminated by MeOH

Fullerene-crosslinked polymer gels

A sol–gel transformation occurred when the grafting reaction (reactions 1–3 of Scheme 1) was carried out at a high molar ratio of Bu^sLi to C_{60} (*i.e.* $[Bu^sLi]/[C_{60}] > 1$). The mass% of C_{60} incorporation into the fullerene containing polymers was measured by TGA analyses. Fig. 4 shows the mass loss for both the pristine *cis*-1,4-polybutadiene [curve (*a*)] and the C_{60}-crosslinked polybutadiene elastomer [curve (*b*)]. Comparing curve (*b*) with curve (*a*) of Fig. 4 shows that polybutadiene backbones in the C_{60}-containing polymer sample completely decomposed at 350–500 °C with no mass loss for C_{60} up to 650 °C. As a result, about 51 mass% incorporation of C_{60} was obtained.

The degree of swelling for the as-synthesized C_{60}-crosslinked *cis*-1,4-polybutadiene in benzene was determined according to: (wet mass − dry mass)/dry mass,[35] from which a value of about 9000% was obtained for the sample with 51 mass% C_{60} incorporation. The resultant dry C_{60}-crosslinked *cis*-1,4-polybutadiene elastomers were studied by high-resolution solid-state NMR spectroscopy, and the results are shown in Fig. 5. A single 90° pulse sequence with a repetition time of 2 s, together with MAS–DD techniques, was used to measure the ^{13}C spectra for the pristine *cis*-1,4-polybutadiene and mobile regions of the C_{60}-crosslinked polybutadiene, as the resonances from C_{60} or rigid domains adjacent to C_{60}-crosslinking sites were unobservable due to long ^{13}C relaxation times.[36] The ^{13}C signals of C_{60} and those polybutadiene segments near to the C_{60}-crosslinking sites were, however, detected by the cross-polarization (CP) method under MAS–DD conditions. In this case, the ^{13}C resonances from mobile segments in the C_{60}-crosslinked polymer sample became unobservable due to their weak capability of cross-polarization, as also was the case for the pristine (amorphous) *cis*-1,4-polybutadiene. For comparative purposes, Fig. 5(*a*) and (*b*) show the MAS–DD ^{13}C NMR spectrum for the pristine *cis*-1,4-polybutadiene and the C_{60}-crosslinked polybutadiene,

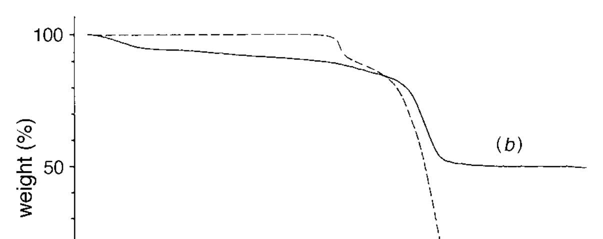


Fig. 4 TGA mass loss data of (*a*) *cis*-1,4-polybutadiene; (*b*) C_{60}-crosslinked *cis*-1,4-polybutadiene. Scanning rate, 10 °C min^{-1}.

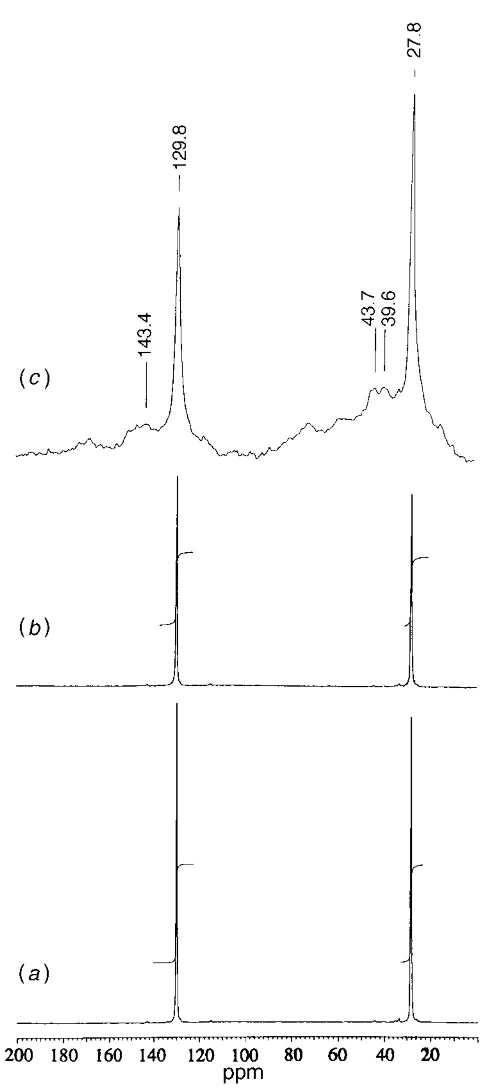


Fig. 5 Solid state ^{13}C NMR spectra of (*a*) the unreacted *cis*-1,4-polybutadiene (MAS–DD); (*b*) C_{60}-crosslinked *cis*-1,4-polybutadiene (MAS–DD); (*c*) C_{60}-crosslinked *cis*-1,4-polybutadiene (CP–MAS–DD)

respectively. The similar overall appearance of the narrow resonances seen in Fig. 5(*a*) and (*b*) indicates that the major contribution to the mobile regions in the C_{60}-crosslinked sample is from those non-crosslinked or lightly crosslinked polybutadiene segments. The ratio of aliphatic carbons to olefinic carbons was assessed by integration of the resonance peaks at 27.8 and 129.8 ppm.[31] This ratio was found to reduce from 1.00 [Fig. 5(*a*)] to 0.95 [Fig. 5(*b*)] upon grafting with C_{60}, indicating, once again, that C_{60} was grafted onto the aliphatic carbons. Assuming that the loss of the aliphatic carbon resonance at 27.8 ppm resulted fully from the grafting reaction, it can be estimated that the percentage incorporation of C_{60} should be about 57 mass% for a mono-addition, 40 mass% for a bis-addition, and 30 mass% for a tris-addition onto each of the C_{60} entities. The observed value of 51 mass% from the TGA measurement on the crosslinked sample, which was also used for the NMR measurement, indicates that the polymer-gel contains a significant amount of mono-functionalized C_{60} dangling groups in addition to various multi-attached fullerenes at the crosslinking sites. These mono-functionalized C_{60} pendant groups should allow the final product to retain the physicochemical properties characteristic of C_{60}.

The ^{13}C CP–MAS–DD spectrum of the C_{60}-crosslinked polybutadiene (Fig. 5(*c*)) shows rather wide linewidths for almost all resonances, suggesting a broad chemical-shift isotropic distribution of the resonances associated with rather rigid regions. Several new resonances were also observed as compared to Fig. 5(*b*). The resonances at 43.7 and 39.6 ppm are attributed to the aliphatic carbons at and next to the C_{60}-grafting sites, respectively, as shown in the structural unit of $-CH(C_{60})-CH_2-$.[31,32] The band with a chemical shift around 143.4 ppm was assigned to unreacted olefinic carbons on the polymer-bound C_{60} moieties.[26,37,38] The appearance of weak resonances at about 71.9 and 168.4 ppm may suggest a partial conversion of the polymer-bound fullerenes to fullerols (see below) and further rearrangements to ketone–hemiketal moieties.[37–40]

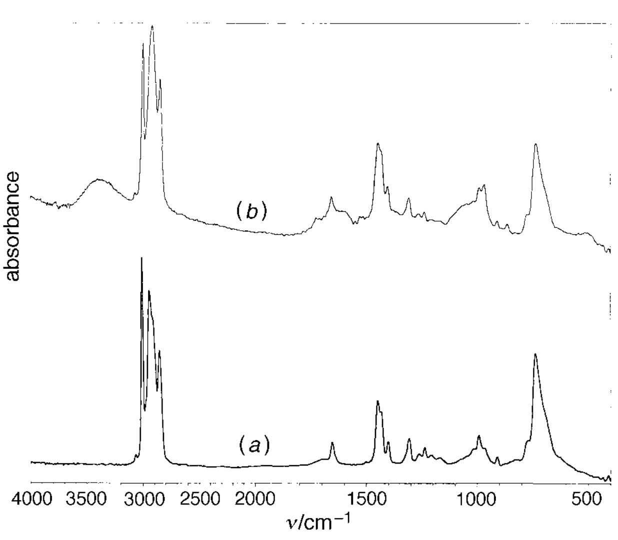


Fig. 6 FTIR spectra of (*a*) the pristine *cis*-1,4-polybutadiene; (*b*) C_{60}-grafted *cis*-1,4-polybutadiene terminated by an undegassed aqueous HCl (36 mass%)–MeOH solution (1 : 1 v/v)

Fullerol-containing polymers

Previously reported syntheses of fullerols from fullerenes have involved the use of strong acids, such as sulfuric acid and nitric acid, at a relatively high temperature (typically, 85–115 °C).[34,37–42] However, we found that an aqueous HCl–methanol solution is an efficient reagent for the conversion of the polymer-bound fullerenes to fullerols even at room temperature. Fig. 6 reproduces FTIR spectra for *cis*-1,4-polybutadiene before and after the C_{60}-grafting, followed by quenching with an undegassed aqueous HCl(36 mass%)–MeOH (1 : 1 v/v) solution (Method 1). Comparing spectrum (*b*) with (*a*) of Fig. 6 shows a strong hydroxy absorption band around 3400 cm^{-1}, together with several other new absorption bands characteristic of fullerols centred at 1595, 1392 and 1084 cm^{-1}.[37]

Further evidence for the C_{60} grafting reaction and/or the subsequent conversion from the polymer-bound fullerenes to fullerols was obtained by NMR measurements. The solution ^{1}H NMR spectra for the pristine *cis*-1,4-polybutadiene and a soluble C_{60}-grafted *cis*-1,4-polybutadiene after having been terminated by an undegassed aqueous HCl–MeOH solution are given in Fig. 7. By referring to Fig. 7(*a*), the peaks at 2.08 and 5.40 ppm seen in Fig. 7(*b*) correspond to the aliphatic and olefinic protons in the *cis*-1,4-polybutadiene chains.[31] The weak, broad peaks centred at about 2.70 and 5.60 ppm may be attributed to the expected aliphatic and olefinic proton resonances of $-CH(C_{60})-$ and $=CH-C(C_{60})-$, respectively. The observed downfield shift for these ^{1}H NMR peaks of the 1,4-polybutadiene upon grafting with C_{60} is consistent with an electron-withdrawing influence from the grafted fullerenes.[5,6] The broad bands centred at *ca.* 3.95 ppm may arise from those hydroxy protons on the polymer-bound fullerols.[37–40] The sharp peaks at about 7.25 and 3.40 ppm are attributable to impurities associated with $CHCl_3$ and MeOH, respectively.[32]

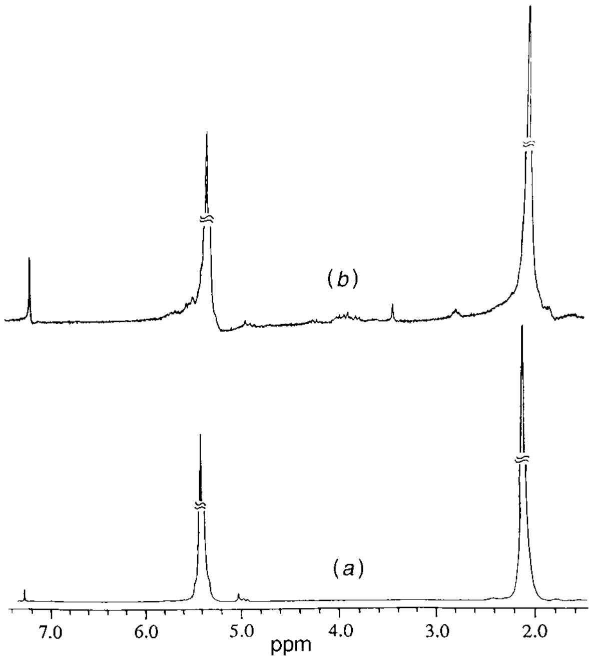


Fig. 7 ^1H NMR spectrum, measured in $CDCl_3$, of (*a*) *cis*-1,4-polybutadiene; (*b*) soluble C_{60}-grafted *cis*-1,4-polybutadiene terminated by an undegassed aqueous HCl (36 mass%)–MeOH solution (1 : 1 v/v)

The above results prompted us to investigate the conversion between the polymer-bound fullerenes to fullerols in a more controllable manner by using the C_{60}-grafted polybutadiene after having been terminated with MeOH (*i.e.* Product **IV** of Scheme 1) as the starting material for the treatment in an aqueous HCl–MeOH solution (Method 2). Fig. 8 shows FTIR spectra for the MeOH-terminated C_{60}-grafted polybutadiene before and after the acid treatment. As mentioned above, the broad absorption peaks centred at 1470, 1140 and 500 cm^{-1} seen in Fig. 8(*a*) characterize the polymer-bound fullerene C_{60} in the starting material. Upon treating it with an undegassed aqueous HCl (36 mass%)–MeOH (1 : 1 v/v) solution at room temperature [Fig. 8(*b*)], the strong hydroxy absorption bands characteristic of fullerols developed, notably at 3424 and 1084 cm^{-1}, while the bands centred at 1470, 1140 and 500 cm^{-1} corresponding to the polymer-bound C_{60} decreased significantly. As a control, the same acid treatment was carried out on the lithiated, fullerene-free polybutadiene, after it had been quenched by MeOH in the same manner as for the C_{60}-grafted polybutadiene. No change in the FTIR spectrum with respect to that of the pristine polybutadiene was observed. Therefore, Fig. 8 clearly suggests a conversion from fullerenes to fullerols for the unsymmetrically perturbed, polymer-bound C_{60} under the mild conditions. Prolonged acid treatment, however, may cause subsequent rearrangements from the newly formed fullerols to ketone–hemiketal moieties.[37–40]

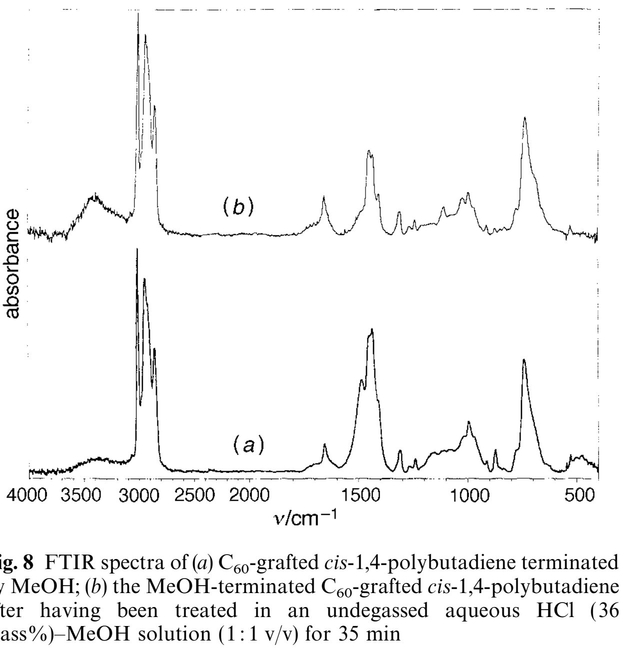


Fig. 8 FTIR spectra of (*a*) C_{60}-grafted *cis*-1,4-polybutadiene terminated by MeOH; (*b*) the MeOH-terminated C_{60}-grafted *cis*-1,4-polybutadiene after having been treated in an undegassed aqueous HCl (36 mass%)–MeOH solution (1 : 1 v/v) for 35 min

Conclusions

In summary, we have demonstrated that fullerene-functionalized polydienes with multiple pendant fullerenes dispersed along their polymer backbones can be prepared by firstly lithiating polydienes with Bu^sLi, which was followed by covalently grafting C_{60} onto the lithiated polymer chains. Both highly soluble C_{60}-grafted polymers and C_{60}-crosslinked polydiene elastomers can be prepared by properly controlling the reaction conditions. Furthermore, an aqueous methanol solution of hydrochloric acid is shown to be an efficient reagent for the conversion of the polymer-bound fullerenes to fullerols at room temperature.

Given that the lithiation reaction is a very versatile method for preparation of organolithium materials,[43] the grafting reaction described in this paper should have important implications for covalent grafting of fullerenes onto various polymer chains.[44–46] While the soluble and/or crosslinked fullerene-containing polymers thus prepared may open up novel applications for the fullerenes, the acid treatment is expected to be of use for making a wide range of new polymer-modified fullerene derivatives from the fullerol-containing polymers *via* reactions characteristic of hydroxy groups.

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