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Viscoelastic behavior of fullerene end-capped linear polymers

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Abstract

Viscoelastic behavior of C_{60}-end-capped linear polybutadiene and C_{60}-end-capped poly(butadiene-*co*-styrene) with molecular weight (M_n) ranging from 30 to 130 kg/mol and with polydispersity index (M_w/M_n) ranging from 1.02 to 1.08 was investigated. These polymers were synthesized through anionic polymerization of butadiene and styrene in hexane, in which the living ends were capped with the C_{60} via an alcoholate bridging. Rheological measurements showed that the polymer dynamics in the terminal zone were profoundly affected by the presence of fullerene, while the dynamics in the entanglement-plateau and at the terminal relaxation were nearly unaffected.

Keywords: Fullerene tethered polymers; Viscoelastics; Entanglement

Covalent attachment of fullerene to specific polymers may allow a combination of the nano-sized allotropic globular characteristics of fullerene with those of the polymer matrix [1–3]. Over the past decade, considerable advance has been made in this direction. Many fullerene tethered polymers were designed and synthesized, such as the comb-shaped fullerene polymers [4–8], the main-chain fullerene polymers [9–11], the star-shaped fullerene polymers [12–16], the dendritic fullerene polymers [17,18], and the end-capped fullerene polymers [19–24]. Applications of those polymers have been found in a number of advance fields, including the photoconductivity [20–24], the solar energy conversion [25–28], the nonlinear optics [29–31], and the improved mechanical stability [32]. Although a large amount of work was done on the electro-optical properties of those polymers, little attention was paid on the rheological properties and processing characteristics of those materials. In this communication, we investigate the viscoelastic behavior of the simplest case, in which the fullerene ball is end-capped to a polymer chain. We intend to address several important issues pertaining to the C_{60}-tethered polymers. First, does the presence of C_{60} in a polymer chain affect the entanglement? Second, does the presence of C_{60} in a polymer chain affect the terminal time τ_t? Third, does the presence of C_{60} affect the dynamic behavior of the polymer in the terminal zone? From a fundamental point of view, fullerene end-capped polymers should represent interesting model systems for elucidating our knowledge about the mechanistic details of chain-like molecules in melts.

Fullerene ball, due to electron-deficiency, readily reacts with nucleophiles [5,33,34]. The synthesis concept of C_{60} end-capped polymer in this study was based on the reaction of an anionic living polymer chain with C_{60}. However, such a reaction could be complicated by multiple chain substitution [12–14], which would result in a mixture of various derivatives. In order to prevent multiple chain substitution, the reaction was chemically modified through switching the highly reactive anionic carbonion to a low reactive alcoholate before performing C_{60}-capping reaction. Such a modification is important for it allows the fullerene ball to be attached by one polymer chain in hexane solutions (see Fig. 1). The description of the reaction of alcoholates with C_{60} can be found elsewhere [33].

The carbonion living polymer was prepared in a stainless steel reactor in which the monomer (butadiene and styrene)

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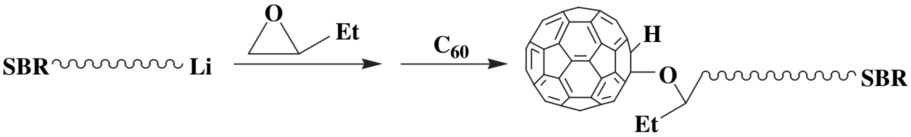

Fig. 1. Synthesis of C_{60} end-capped polymer.

concentration was about 10% and the solvent (hexane) concentration was about 90%. The temperature of the reactor was set to 50 °C. Once the temperature stabilized, a pre-determined amount of butyl-lithium (initiator) and 2-bis(2′-tetrahydrofuranyl) propane (randomizer) was charged into the reactor. After about 60 min when the reaction was completed, one portion of the living polymer solution was terminated with isopropanol, which was used as the control. Another portion of the living polymer was further reacted with 1,2-epoxybutane for 30 min at 50 °C, and then reacted with a fullerene solution (0.01 M, in dichlorobenzene), where a ratio of 1:1 C_{60}/polymer chain was used. After an additional 30-min reaction, the C_{60}-tethered polymer was also terminated with isopropanol. Finally, the C_{60} functionalized and the non-functionalized polymers were stabilized with about 0.01% of di-*t*-butyl-*p*-cresol, dried in vacuum, and then stored in a freezer for usage.

The polymers synthesized according to the present method were analyzed by GPC, NMR, and DSC techniques. GPC measurements were carried out in tetrahydrofuran (THF) solution using polystyrene as the standard. The molecular weight and functionality were detected using RI and UV detectors, respectively. Monosubstituted C_{60}–polymer exhibited characteristic UV bands in 255, 330 and 430 nm [5,12,19] and a distinguishing (monodispersed) peak in the GPC spectra, which were different from the pure C_{60} and the mixture of derivatives of higher degree substitutions. The analysis showed that the C_{60}–polymers synthesized were all mono-functionalized with C_{60}. The molecular weight of a C_{60}–polymer was slightly larger than that of non-functionalized one (the control). This difference represents the excess exclude volume introduced by the tethered C_{60} structure in THF solutions. The NMR analysis showed the styrene content in the polymer and the vinyl contents in the polybutadiene portion of each polymer. The DSC analysis showed the glass transition temperature (T_g) of each polymer. The results are summarized in Table 1. There are four groups of polymers, coded as BR, C_{60}–BR, SBR, and C_{60}–SBR, which stand for the polybutadiene rubber, the C_{60} end-capped polybutadiene rubber, the poly(styrene-*co*-butadiene) rubber, and the C_{60} end-capped poly(styrene-*co*-butadiene) rubber. The value in the bracket represents the molecular weight. The reason for using diene polymers for this study is that these polymers have good miscibility with fullerene-like particles. An example is tire rubber, in which diene polymers have long been demonstrated as good hosts for carbon black fillers.

Table 1
Molecular characteristics of polymers

Polymer code	M_n (g/mol)	M_w/M_n	Styrene (%)	Vinyl (%)	DSC, T_g (°C)
SBR (70K)	68,980	1.034	13.8	21.9	−67.0
C_{60}–SBR (70K)	72,220	1.077	14.1	21.7	−67.1
SBR (130K)	126,010	1.026	20.0	42.9	−36.3
C_{60}–SBR (130K)	128,320	1.036	20.4	42.2	−35.7
BR (30K)	29,630	1.029	0	65.9	−43.4
C_{60}–BR (30K)	30,900	1.030	0	65.3	−43.3
C_{60}–BR (70K)	72,160	1.023	0	46.1	−54.1

Viscoelastic measurements were conducted in oscillatory shear using a Rheometrics ARES strain-controlled rheometer equipped with dual (200 g cm and 2000 g cm) force rebalance transducers and a RIS orchestrator V656 software. A pair of parallel plates was used in this investigation. The diameter of the plate was 25 mm and the gap between the two plates was about 2 mm. After a polymer was loaded and the normal force was relaxed to zero, the material was allowed to equilibrate at a given temperature before performing a frequency-sweep from $\omega = 0.01$ to 10 Hz. In order to gain a sufficient torque signal, the strain amplitude was selectively ranged from 0.1 to 5%, depending on the material softness. All strains used were within the linear range of the polymer response. Variation of sample fixtures from parallel plates to core/plates did not influence the findings herein. Within the linear range these two types of fixtures gave the same results, but a parallel plate fixture of 2 mm gap was relatively easy to set up and took less time for the loaded polymer to relax. Test temperatures were ranged from −30 to 110 °C with an increment of 10 °C. Master curves were constructed by shifting the temperature–frequency sweep data using the time–temperature superposition (TTS) principle. The reference temperature was chosen to be 30 °C. For all materials investigated, the shifting factors were close to the WLF description, with no significant exception.

Fig. 2 illustrates the behavior with master curves of the storage modulus G' and the loss modulus G'' as functions of frequency for a conventional SBR of 70K molecular weight and for a C_{60}–SBR of 70K molecular weight. For the SBR (70K), the master curves of G' and G'' display an entanglement-plateau at high frequencies and a Newtonian-fluid behavior ($G' \propto \omega^2$, $G'' \propto \omega^1$) at low frequencies. The transition from the plateau zone to the fluid zone occurs at a terminal relaxation time $\tau_t = 1/\omega_t$ at which the G'' passes through a maximum. For the C_{60}–SBR (70K), the storage modulus G' also displays an entanglement-plateau at high frequencies. The height and the width of the entanglement-plateau of the C_{60}–SBR (70K) are essentially the same as those of the SBR (70K). The loss modulus G'' spectrum of the C_{60}–SBR (70K) around the transition matches the spectrum of the SBR (70K) (see the inset in Fig. 2). The terminal relaxation time τ_t of C_{60}–SBR (70K) is also the same as that of SBR (70K). This behavior suggests that the presence of C_{60} in a chain end

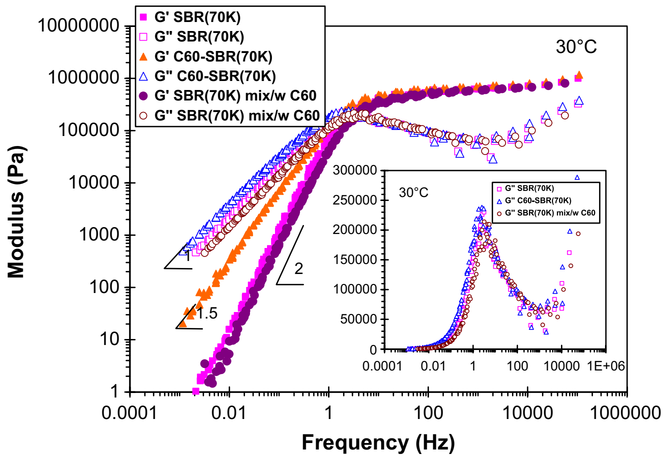

Fig. 2. Master curves of the storage modulus G' and the loss modulus G'' as functions of frequency for C_{60}–SBR (70K), SBR (70K) and a mixture of C_{60} and SBR. The inset shows the G'' spectrum in a semi-logarithmic plot.

does not affect the entanglement of the polymer. However, the presence of C_{60} significantly affects the polymer dynamics at low frequencies. The low frequency slope of the C_{60}–SBR (70K) in the $\log G'$ vs $\log \omega$ spectrum is approximately 1.5 in comparison to a typical slope of 2 for a Newtonian-fluid. In addition, such a non-Newtonian behavior of C_{60}–SBR covers a wide range of frequencies of about four decades. At present, there is no clear sign of whether the C_{60}–polymer will return to Newtonian-fluid behavior at even lower frequencies. However, further lowering the frequency has exceeded the range of experimental capability, and also further increase of temperature using TTS principle will result in the diene–polymer decomposition. In the same range, the loss modulus G'' of the C_{60}–SBR (70K) still follows the law of $G'' \propto \omega^1$. The zero-shear viscosity η of the C_{60}–SBR (70K) is slightly higher than that of SBR (70K) because the G'' of the C_{60}–SBR (70K) is slightly higher than that of the SBR (70K) and $\eta = G''/\omega$ at low frequencies.

The effect of chain length (or molecular weight) on the rheology of the C_{60}-tethered polymers is presented in Fig. 3. Again, the presence of C_{60} in a polymer chain has no significant effect on the entanglement-plateau and the terminal time. The non-Newtonian behavior of a C_{60}–SBR at low frequencies, however, is significantly influenced by the chain length. For example, the frequency slope of the C_{60}–SBR (70K) in the $\log G'$ vs $\log \omega$ spectrum at low frequencies is about 1.5, but the frequency slope of the C_{60}–SBR (130K) in the $\log G'$ vs $\log \omega$ spectrum is about 1.8. Apparently, the non-Newtonian behavior of a C_{60}–SBR at low frequencies decreases as the polymer molecular weight increases. The effect of the chemical composition of the polymer chain is shown in Fig. 4. Apparently, at low frequencies the dynamics of a C_{60}-tethered polybutadiene or C_{60}–BR is closer to a Newtonian-fluid than that of a C_{60}-tethered poly(butadiene-*co*-styrene) or C_{60}–SBR. The frequency slope of C_{60}–BR (30K) at low frequencies in the $\log G'$ vs $\log \omega$ spectrum is about 1.8, and the frequency slope of C_{60}–BR (70K) is about 2, in comparison to that of C_{60}–SBR (70K) which is about 1.5.

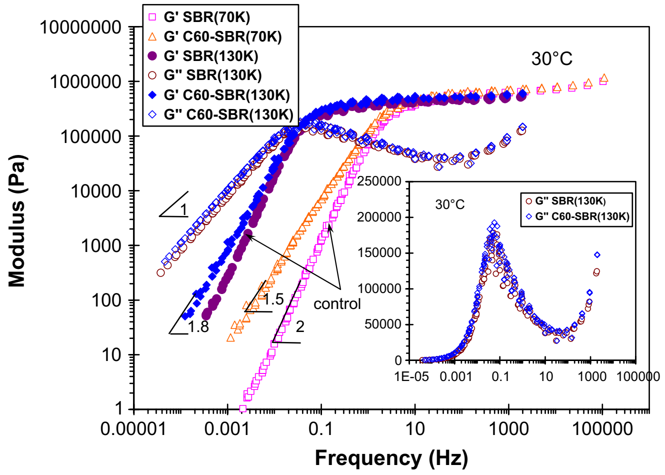

Fig. 3. Master curves of the storage modulus G' and the loss modulus G'' as functions of frequency for C_{60}–SBR and SBR of various chain lengths. The inset shows the G'' spectrum in a semi-logarithmic plot.

The effects of C_{60} on the dynamics of polymer chains in melts as described above cannot be interpreted in terms of existing theories [35–39]. First, the viscoelastic behavior in the terminal zone corresponds to the continuous resumption of random average configurations of the macromolecular coils that have completely freed from the entanglement constraints. The presence of C_{60} in a polymer chain apparently introduces an effect that increases the internal barrier on the friction between polymer chains as the shear frequency decreases. This effect depends not only on the detailed monomer structures of the chain but also on the molecular weight of the polymer. The reptation or tube model [35,36], though has provided us with a framework for understanding of transport properties in entangled linear polymers, cannot provide a satisfactory explanation to the phenomena observed. Second, the filler effect of the C_{60} particles in the SBR matrix at such a low concentration (about <1 wt%) would not be sufficient to result in the polymer matrix becoming non-Newtonian at low

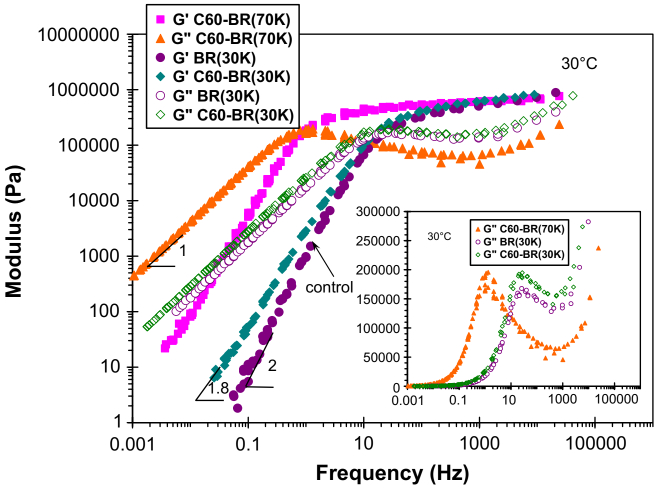

Fig. 4. Master curves of the storage modulus G' and the loss modulus G'' as functions of frequency for C_{60}–BR and BR of various chain lengths. The inset shows the G'' spectrum in a semi-logarithmic plot.

frequencies [37,38]. To confirm this point of view, we tested a mixture that contained the SBR (70K) and C_{60} in a ratio that was similar to that used in synthesis of the C_{60}–SBR (70K). The mixture was prepared by dissolving both the polymer and C_{60} in toluene, mixed thoroughly on a roller mixer for two days, and then vacuum-dried for one week to completely evaporate the solvent. This mixture, coded as SBR (70K) mix/w C_{60} (see Fig. 2), shows the same rheology as that of the pure SBR. This experimental result suggests that simply mixing C_{60} and SBRs will not change the rheology of conventional SBRs. The unusual non-Newtonian behavior must be associated with the dynamics of the C_{60}-end-capped polymer chains. In addition, Fig. 2 shows that the addition of pure C_{60} into the SBR matrix brings in a plasticizer-like effect as the viscosity ($\eta = G''/\omega$ at low frequencies) and the terminal relaxation time ($\tau_t = 1/\omega_t$ where the G'' passes through a maximum) of the SBR–C_{60}-mixture are all slightly lower than that of the pure SBR. Third, it is unlikely that the C_{60}–polymer clustering would adequately explain this effect. The reason is that a cluster, once formed, will act like a star polymer. The branched nature of a cluster should have a profound effect on the plateau region dynamics [39–41] and should lead to a prolonged terminal relaxation time. Also, the clustering effect should decrease as test frequency decreases because the cluster formation and break-up are transient in nature. However, the observation that the attachment of C_{60} to a polymer chain has essentially no effect on the plateau region and no effect on the terminal relaxation time makes it doubtful that C_{60}–polymer clustering could be the explanation. Furthermore, addition of pure C_{60} into the SBR reduces the viscosity and the terminal relaxation time when compared to pure SBR (see Fig. 2), suggesting that pure C_{60} in SBR behaves like solvent molecules.

We do not yet know the reason, but we speculate that the non-Newtonian behavior of C_{60}–polymer at low frequencies may stem from the asymmetric structure of the chain. Recent study on the microbead-tethered DNA has shown that the bead has an effect on the dynamics of the whole chain [42]. If this is the case, the asymmetric effect will minimize as the chain is lengthened, and will intensify as the C_{60}–polymer chain is shortened. Once the chain is locked by entanglement, the asymmetric character of the chain is lost and only the dynamics at a length scale that is shorter than the entanglement length becomes important. Our experimental results (as shown in Figs. 2 and 3) seem to support the hypothesis that the asymmetric characteristic of the chain decreases as the chain length increases. Nevertheless, we hope that future theoretical advances can help to resolve this problem.

In summary, we studied the viscoelastic behavior of fullerene (C_{60}) end-capped linear polymers, such as the C_{60}–polybutadiene and C_{60}–poly(butadiene-*co*-styrene). These polymers were synthesized through anionic polymerization of butadiene and styrene in hexane, where the living ends were capped with the C_{60} via an epoxybutane bridging. Rheological measurements showed that the polymer dynamics at the terminal zone were profoundly affected by the presence of fullerene, while the dynamics in the entanglement-plateau and the terminal relaxation time of the polymer were nearly unaffected. This phenomenon cannot be interpreted in terms of existing models.

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