semidilute regime using eq 10 and 11 is equivalent to relation 12.

In summary, from the viscoelastic data available in the literature, the numbers of entanglement strands per cubed tube diameter for different linear flexible polymers are calculated. In agreement with the expectation based on the universality of the tube model, the obtained n_t values are very constant. This supports that the topological effect as described by the tube model is dominant in affecting the viscoelastic properties of polymers. In the semidilute regime, chain entanglement is greatly influenced by the thermodynamic property: excluded volume effect, in the solution. In the melt (and the concentrated region), packing the space with polymer segments (and solvent molecules) appears to be the dominant factor in determining chain entanglement as suggested by eq 7.

With n_t being constant, a link between polymer viscoelastic behavior and polymer chain microstructure has been made.

The result that n_t is quite large explains the conclusion that the tube renewal process is negligible as long as the MWD is very narrow, which was previously drawn from the linear viscoelastic spectrum line-shape analyses.

Note. The main idea presented in this paper is quite different from that of Graessley and Edwards. A Referee pointed out "A consequence (of the Graessley–Edwards analysis) is that a melt of a bulky polymer with large side groups should behave the same as a less bulky polymer at somewhat less than melt concentration. Thus the Graessley–Edwards analysis would lead one to expect essentially no dependence of n_t on C in the concentrated regime, in contradiction to eq 9". Some readers may have a similar question. The answers to the Referee's comments listed below, I think, would help explain why this work and what are the possible defects in the Graessley–Edwards analysis.

(1) As explained in the main text, the Graessley–Edwards relation is, at best, an approximation.

(2) The present correlation (eq 4) is much stronger than that of Graessley and Edwards. Compared to experimental results, their relation has a standard deviation of $\sim 30\%$ (see Table I of ref 16); while it is only 8% in the present case.

(3) The connection between melts and concentrated solutions, which the referee pointed out as the main thrust of the Graessley–Edwards analysis, is in fact not that well supported by the experimental results. One can easily draw a straight line with a slope as large as 3 or higher (the a value of eq 4 of ref 16) through the more reliable data points (mainly those of the hydrocarbon polymers) in Figure 1 of ref 16. On the other hand, the a value in the concentrated solution systems is typically between 2 and 2.3. (from the relation $G_N \sim C^a$). This large discrepancy is, of course, related to the two previous points.

(4) The tube diameter can be calculated from the entanglement molecular weight (which is calculated from the measured plateau modulus, density, and temperature) and the characteristic ratio; and thus is a well-defined, fundamental, physical quantity in the Doi-Edwards theory. This quantity is totally missing in the Graessley–Edwards relation (eq 4 of ref 16). This seems quite inconsistent with the success of the Doi–Edwards theory.

Note Added in Proof. From L. J. Fetters, I have received a collection of data twice as large as that in Table I, much of which is unpublished and has been accumulated over years with his co-workers. They have calculated the n_t values from their data and confirm the conclusion that n_t is topologically a universal constant. Their results are being prepared for publication (private communication).

Registry No. Polystyrene, 9003-53-6; poly(α-methylstyrene), 25014-31-7; polybutadiene, 9003-17-2; polyisobutylene, 9003-27-4; polyisoprene, 9003-31-0; poly(vinyl acetate), 9003-20-7; polyethylene, 9002-88-4; poly(methyl methacrylate), 9011-14-7; poly(hexyl methacrylate), 25087-17-6; poly(octyl methacrylate), 25087-18-7; poly(ethylene oxide), 25322-68-3; poly(2-ethylbutyl methacrylate), 25087-19-8.

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Nitroso Spin Labeling of Polymers Containing Main Chain Double Bonds: An Electron Spin Resonance Study

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Introduction

The synthesis and ESR spectroscopy of nitroxyl-labeled polymers have received considerable attention during the last 15 years. The methods of preparation and the possible applications have been reviewed by Törmälä,[1] Miller,[2] and recently by Cameron and Bullock.[3] The most frequently used method for bonding a stable radical center of nitroxyl type to a polymer backbone or side chain is based on the

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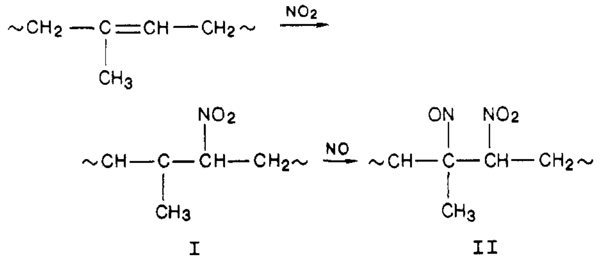
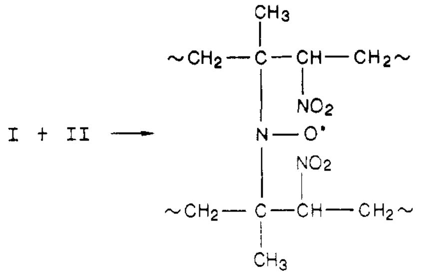
condensation reaction between functionalized cyclic nitroxyl radicals and functionalized polymers (e.g., those carrying hydroxyl, amino, carboxyl, or acid chloride groups).[4-8] The homo- and copolymerization methods of spin labeling by using nitroxyl-type or nitroxyl-precursor monomers have also been applied with success, although the degree of polymerization is rather limited in most cases.[9-15] Spin trapping of macroradicals created by hydrogen abstraction from polymer chains is also a viable route, especially in the case of nonfunctionalized polymers.[16-18] For polymers carrying ketonic carbonyl groups, the Keana synthesis is an excellent way to produce spin-labeled macromolecules.[19] Other methods of chemical modification of macromolecular substances are also known, e.g., end labeling of polymers by spin trapping the propagating polymer chain.[20,21]

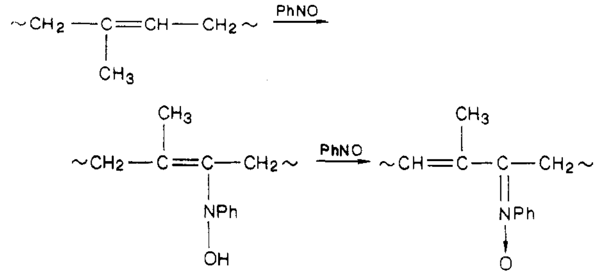
In a previous paper, we described a special kind of spin labeling which is based on the observation that nitrogen oxides form nitroxyl radicals in the reaction with macromolecular chains containing C=C double bonds:[22]


(1)

$$\sim CH_2-\underset{CH_3}{C}=CH-CH_2\sim \xrightarrow{NO_2} \underset{\text{I}}{\sim CH-\overset{NO_2}{\underset{CH_3}{C}}-CH-CH_2\sim} \xrightarrow{NO} \underset{\text{II}}{\sim CH-\overset{ON}{\underset{CH_3}{C}}-\overset{NO_2}{CH}-CH_2\sim} \quad (1)$$


(2)

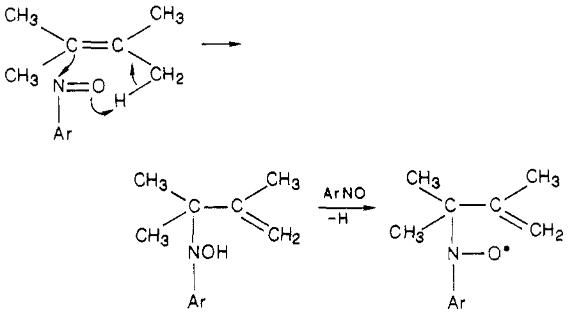
In this paper, we propose another easy way of obtaining nitroxyl spin-labeled macromolecular chains from the same polymers, i.e., appropriate homo- and copolymers that contain diene monomer units incorporated into the backbone.[22] On the basis of the results concerning the addition reactions of aromatic C-nitroso compounds with olefins,[23-33] we attempted to carry out an analogous reaction with unsaturated polymers. In fact, up to now a considerable amount of research work has been devoted to clarify the mechanism of reaction between different nitrosobenzenes and olefins.[23,27,29] The pioneering studies were made by Alessandri,[23] who interpreted the reaction between nitrosobenzene and the C_5H_8 unit in rubber by the following scheme:


(3)

$$\sim CH_2-\underset{CH_3}{C}=CH-CH_2\sim \xrightarrow{PhNO} \sim CH_2-\overset{CH_3}{C}=\underset{\underset{OH}{NPh}}{C}-CH_2\sim \xrightarrow{PhNO} \sim CH=\overset{CH_3}{C}-\underset{\underset{O}{\overset{\|}{NPh}\downarrow}}{C}-CH_2\sim \quad (3)$$

In the cited paper, there is no indication of any nitroxyl radical formed.

An alternative mechanism proposed by Sullivan for the case of 2,3-dimethylbut-2-ene explains the formation of nitroxyl radical via the intermediate N,N-disubstituted hydroxylamine that undergoes further oxidation by the aryl-nitroso compound:[27]


(4)

where Ar stands for substituted phenyl ring. Recently Sutcliffe and Zilnyk reported an analogous mechanism for the reaction of nitroso compounds with long-chain normal 1-alkenes and cyclohexene.[33]

Experimental Section

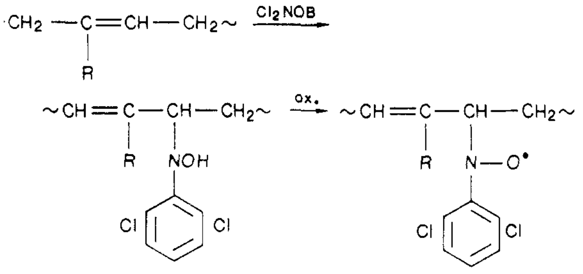
Three different diene polymers, namely polybutadiene ($\bar{M}_n$ = 87 000; 98% cis), polyisoprene ($\bar{M}_n$ = 180 000; 96% cis, synthetic), and poly(isoprene-*co*-isobutylene)/butyl rubber ($\bar{M}_n$ = 61 000, 12 000, and 2000 fractions; 2.5% isoprene content), were used in the spin-labeling experiments with 2,6-dichloronitrosobenzene. The latter compound was prepared from 2,6-dichloroaniline (Merck-Schuchardt) by the method of Holmes and Bayer.[34]

Toluene solutions of the polymers (50 g/1000 cm^3) and 2,6-dichloronitrosobenzene (10^{-2} M) were prepared separately and then mixed in ESR sample tubes in different volume ratios. After deaeration by argon bubbling, the ESR spectra were recorded repeatedly.

The ESR spectrometer employed was a JEOL-FE-3X instrument operating in X-band with 100-kHz modulation frequency. The variable-temperature accessory (JEOL) controlled the cavity temperature with an accuracy of 1 °C.

Results and Discussion

For all polymers under study the addition of the nitroso compound gives rise to a six-line spectra with unequal line amplitudes, which is characteristic of polymer-bound nitroxyl centers with one β-hydrogen. The presence of only one β-hydrogen suggests that in the case of rubber polymers the nitroxyl radical formation proceeds according to the "ene" mechanism mentioned above:[27]


(5)

R = H or CH$_3$

The signal of nitroxyl radical can be observed right after mixing. The concentration buildup, depicted in Figure 1, shows that the rate of nitroxyl formation is in close correlation with the nitroso/polymer concentration ratio during the initial period of the process. This is not the case for the asymptotic concentrations which were achieved approximately 10 h after mixing. The nitroxyl radicals persisted for months in solution stored in sealed ESR tubes at room temperature.

The ESR spectra obtained for the three polymers are shown in Figure 2. In all cases, the six-line pattern can be interpreted as a result of hyperfine splittings by the $^{14}N(I = 1)$ and $^{1}H(I = {}^{1}/_{2})$ nuclei. The ***g*** values are practically the same for all types of macroradicals, whereas

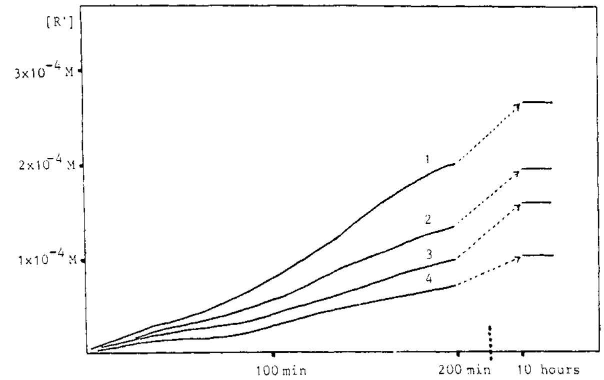


Figure 1. Buildup of polymeric nitroxyl radical concentration in the course of labeling with 2,6-dichloronitrosobenzene. Solvent: toluene. Temperature: 298 K. Initial composition of samples: poly(isoprene-*co*-isobutylene), 10 g/1000 cm^3; 2,6-dichloronitrosobenzene, (1) 7.5 × 10^{-3}, (2) 5.0 x 10^{-3}, (3) 3.7 × 10^{-3}, and (4) 2.5 × 10^{-3} M.

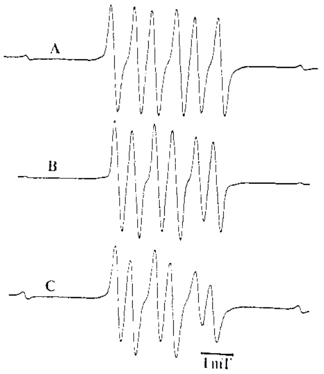


Figure 2. ESR spectra of spin-labeled polymers dissolved in toluene. Deaerated samples were measured at room temperature (298 K): (A) polybutadiene; (B) polyisoprene; (C) poly(isoprene-*co*-isobutylene).

Table I
ESR Parameters of the Polymers Labeled by 2,6-Dichloronitrosobenzene (Solvent, Toluene; Temperature, 298 K)

polymer	g	a_N, mT	a_H, mT
polybutadiene	2.0059	1.274	0.720
polyisoprene	2.0061	1.263	0.526
poly(isoprene-*co*-isobutylene)	2.0060	1.252	0.454

the hyperfine splitting constants depend on the type of labeled polymer (Table I).

The common feature of the spectra is the inequality of line widths which is a consequence of hindered rotational reorientation of the nitroxyl fragment attached covalently to a macromolecular chain. It can clearly be seen from the spectra that the segmental mobility or micro-Brown motion of the three polymers differs noticeably even at room temperature. If the temperature is decreased, this difference becomes more significant. As it is shown in Figure 3, a continuous change of the line shape takes place due to the transition from the motional narrowing region (10^{-11} s $\leq \tau_R \leq 10^{-9}$ s) toward the slow-motional region (10^{-9} s $\leq \tau_R \leq 10^{-6}$ s). τ_R is the correlation time of the rotational diffusion. At 220 K, the spin-labeled butyl rubber gives an asymmetric, broad signal which undergoes further change with decreasing temperature. For instance, at 190 K the distance between the outermost peaks further increases, indicating an enhanced rigidity of the chain. In fact, visual observation reveals that around this temperature the polymer solution is not as transparent as it was originally; i.e., we see a white and hazy suspension in the ESR tube. The other two polymers also achieve this degree of rigidity, but at lower temperatures. The decrease of β-H hyperfine splitting was also detected in all cases.

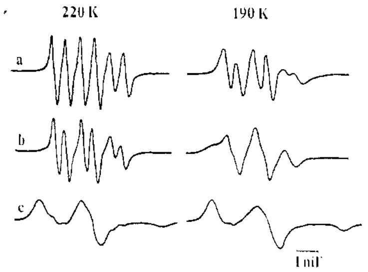


Figure 3. ESR spectra of the spin-labeled polymers at two different temperatures. Solvent: toluene. (a) Polybutadiene; (b) polyisoprene; (c) poly(isoprene-*co*-isobutylene).

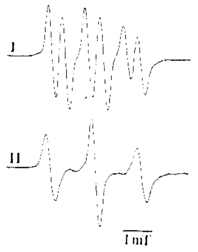


Figure 4. Room-temperature (298 K) ESR spectra of poly(isoprene-*co*-isobutylene) spin labeled in two different ways. Solvent: toluene. (I) Spin labeling with 2,6-dichloronitrosobenzene; (II) spin labeling with nitrogen oxides.

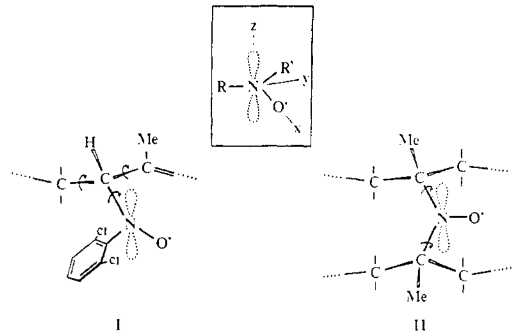


Figure 5. Local mode rotation mobility of the nitroxyl moiety.

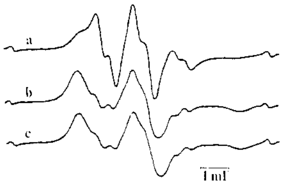


Figure 6. ESR spectra of poly(isoprene-*co*-isobutylene) fractions labeled by using 2,6-dichloronitrosobenzene. Solvent: toluene. Temperature: 298 K. (a) $\bar{M}_n$ = 2000, (b) $\bar{M}_n$ = 12 000, (c) $\bar{M}_n$ = 61 000.

It was pointed out by Freed and his co-workers[35,36] that in the case of a nitroxyl group bound covalently to a polymer backbone, anisotropic rotational diffusion of the radical center takes place. The spectra depend sensitively on the relative orientation of the molecular coordinate system of the nitroxyl moiety with respect to the principal rotation axis of the polymer chain. Indeed, there is a substantial difference in the ESR line shape between the nitroso-labeled butyl rubber (I) and that obtained by using nitrogen oxides (II),[22] as shown in Figure 4. According to the classification of Van et al.,[37] preferential rotation about the y axis seems to take place in case II, whereas in case I the comparison of our spectra with the reported ones in the cited paper[37] suggests a combined rotation about x and y axes (Figure 5).

Furthermore we have observed a significant molecular weight dependence of the line shape. Figure 6 shows three labeled butyl rubber fractions of different $\bar{M}_n$. Their spectra recorded at 220 K indicate that the line shape starts to change markedly only at low molecular weights, which is in accordance with Bullock's finding that the independence of τ_R of the chain length at higher molecular weights is characteristic of a segmental or local mode relaxation.[38]

In summary, the method of nitroso spin labeling offers a simple and versatile route for obtaining nitroxyl functionalized macromolecular chains. The only requirement is the presence of appropriate $C{=}C$ double bonds along the polymer chain. It is to be noted that the so-called forced ideal quasi-living (FIQL) copolymerization method[39,40] provides a particularly good procedure for preparing tailor-made copolymers with controlled composition and molecular weight. By use of this technique, even a very small relative amount of diene as comonomer can be incorporated into the polymer chain in a way that the microstructure of the copolymer, i.e., the sequence distribution along the chain, remains uniform. Another and so far not yet fully exploited feature of the FIQL copolymerization technique is that it works best in producing low molecular weight polymeric species, an inexhaustible pool of starting materials to obtain labeled polymers and macromolecular spin probes.

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Communications to the Editor

Synthesis of Crystalline β-Hydroxybutyrate/β-Hydroxyvalerate Copolyesters by Coordination Polymerization of β-Lactones

Optically active poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate), P(HB-*co*-HV), is manufactured in a fermentation process by ICI and marketed as Biopol through Marlborough Biopolymers, Billingham, U.K.[1] The copolyesters are offered in a range of compositions and are thermoplastics varying in such physical properties as melting point, toughness, and flexibility. Although copolymers containing up to 47 mol % β-hydroxyvalerate (HV) have been isolated,[2,3] the upper limit of HV content obtainable in a high-yield fermentation process is 20–30 mol %.[4]

The P(HB-*co*-HV) system has several remarkable physical properties which make it desirable to explore the entire composition range from 0 to 100% HV. In spite of being random copolymers,[1,5–7] bacterial P(HB-*co*-HV) from *Alcaligenes eutrophus* is crystalline at all accessible compositions.[5,6] Depending upon composition,[5,6] individual copolyesters crystallize in either the poly(β-hydroxybutyrate) (PHB)[8–10] unit cell or the poly(β-hydroxyvalerate) (PHV)[11] unit cell. The lattice transition, at about 30 mol % HV, appears as a pseudoeutectic in plots of melting point and enthalpy of fusion against copolymer composition.[6] This phenomenon of mutually cocrystallizable repeating units, relatively uncommon in polymer science, is called isodimorphism and is a consequence of the similar crystalline conformations of the two homopolymers.

In the present paper we report the synthesis of high molecular weight P(HB-*co*-HV), by a nonbiochemical route, having statistical sequence distributions similar to

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