interactions; this is also the reason for not having investigated any further the role of the effective dielectric constant. We want also to stress that the close resemblance of computed models with models best-fitted to experimental data is obtained without any ad hoc parameter adjustment in the force field adopted. In our view the success of the present approach in tackling the rather severe task of discriminating between the two conformational states (α and γ) of PPVL relies on two factors, both essential: (i) the avoidance of unnecessary restrictions and artifacts, by means of simultaneous optimization of intra- and intermolecular interactions in Cartesian coordinates; (ii) the use of Allinger's force field, of which only the electrostatic part has not been fully tested in the present study due to the specific features of the PPVL system.

The results of the present work are very promising in view of the possible application of our computational procedure for generation of reliable starting models, in dealing with unknown crystal structures, to be further refined by experimental diffraction data.

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Registry No. PPVL (homopolymer), 24969-13-9; PPVL (SRU), 24937-51-7.

Studies on Spin-Labeled Poly(*n*-butyl isocyanate)

Roberto Olayo and Marco A. Patron

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa,
Apartado Postal 55-534, 09340 Mexico D. F.

Wilmer G. Miller*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

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ABSTRACT: The stiff-chain polymer poly(*n*-butyl isocyanate) was labeled with the nitroxide 3-carbamoyl-PROXYL covalently positioned at the main-chain terminus. ESR spectra were measured as function of solvent composition and temperature using carbon tetrachloride, a good solvent, and benzene, a poor solvent. In the dry solid the nitroxide exhibits little motion up to 25 °C but rapidly gains motion and by 60 °C is motionally narrowed. Addition of small amounts of either solvent at any temperature gives rise to bimodal nitroxide relaxation times, one characteristic of the dry polymer at that temperature and the other characterizing a fast motion of 0.02–0.2-ns relaxation time. These results are correlated with side-chain motion as observed by ^{1}H NMR and known mechanical, thermal, and morphological properties of the polymer. The effect of diluent or temperature on side-chain motion has a corresponding effect on the motion of the nitroxide positioned at the end of the main chain.

Introduction

Nitroxide spin labeling of synthetic polymers has been shown to be a useful tool in the study of the motion of polymers under different conditions.[1] Most of the work on labeled rigid rodlike polymers has been done with poly(amino acids),[2–6] where the labels were attached either to the side chain or to the end terminus of the main chain. Information concerning the motion of the rod can be limited by the internal rotation about the bonds between the nitroxide and the main chain; therefore, in the case of the side-chain-labeled polymer, the quantitative interpretation of the EPR spectra describes the nitroxide movement and only limited conclusions can be obtained with respect to the polymer. End-labeled rods have lead to a more specific understanding of the rotational motion about the long axis of the rod.[6] Properties of polyisocyanates such as viscosity,[7,8] dynamics,[9–11] and phase behavior[12,13] have been determined. We have spin-labeled molecules of poly(*n*-butyl isocyanate) (PBIC) with a nitroxide label and present here the study of the polymer as a function of temperature and concentration in different solvents.

Experimental Section

Preparation of Spin-Labeled Polymer. The polymer was prepared by a procedure similar to Shashoua et al.[14] using *n*-butyl isocyanate (Eastman) as monomer in DMF (Merck). Both

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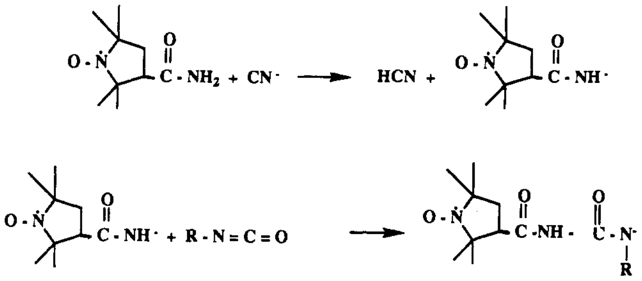

Figure 1. Proposed mechanism of incorporation of the spin label into the polymer.

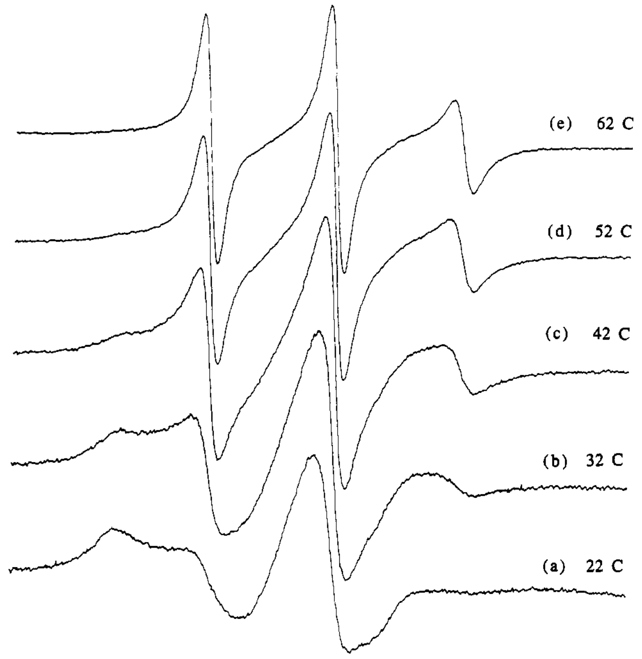

Figure 2. Temperature dependence of the ESR spectra of the pure labeled polymer.

were dried with molecular sieves, and the DMF was distilled at high vacuum. NaCN was used as initiator and was suspended in the DMF. The spin label 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxamide (3-carbamoyl-PROXYL, Aldrich Chemical Co.) was also in the DMF in a ratio of label to isocyanate of 1 to 2000 (mol/mol). The monomer was added by distillation, and polymerization was done at −60 °C on a vacuum line evacuated to 10^{-6} Torr to exclude oxygen. The polymer was purified by repeated dissolution in CCl_4 and precipitation with methanol until no ESR signal could be detected in the supernatant. The weight-average molecular weight of the polymer was determined[7] from the intrinsic viscosity in CCl_4. The level of spin labeling was determined by comparison with ESR signal intensities of samples of known concentrations.

Magnetic Resonance Spectra. A Varian E-3 ESR spectrometer equipped with variable-temperature controller was used to measure ESR spectra. It was operated at a microwave frequency of about 9.15 GHz. The spectra were typically recorded in the vicinity of 3.2 kG and with a modulation amplitude of 1 G. ^{1}H NMR spectra were taken on a Nicolet 300-MHz spectrometer.

Solutions for the magnetic resonance experiments were prepared in 5-mm NMR tubes. Concentrations are reported in volume percent. Carbon tetrachloride and benzene (Fisher spectranalyzed) were used as received. Concentrations less than 40% polymer were made by adding the amounts by weight and sealing the tubes after oxygen removal. Then they were tumbled for 2 weeks at 50 °C. Higher concentrations were prepared by absorption of the solvent vapor at ambient temperature.

Results

The weight-average molecular weight of the polymer was determined to be 145 000. From intensity measurements of the spin-labeled polymer in solution and comparison with appropriate standards, one spin label was present per three polymer chains, assuming all chains have approximately the same length. This suggests that the nitroxide occasionally competed favorably with cyanide to initiate a chain, as shown in Figure 1. From the proposed mechanism the nitroxide is attached at the end of the polymer chain.

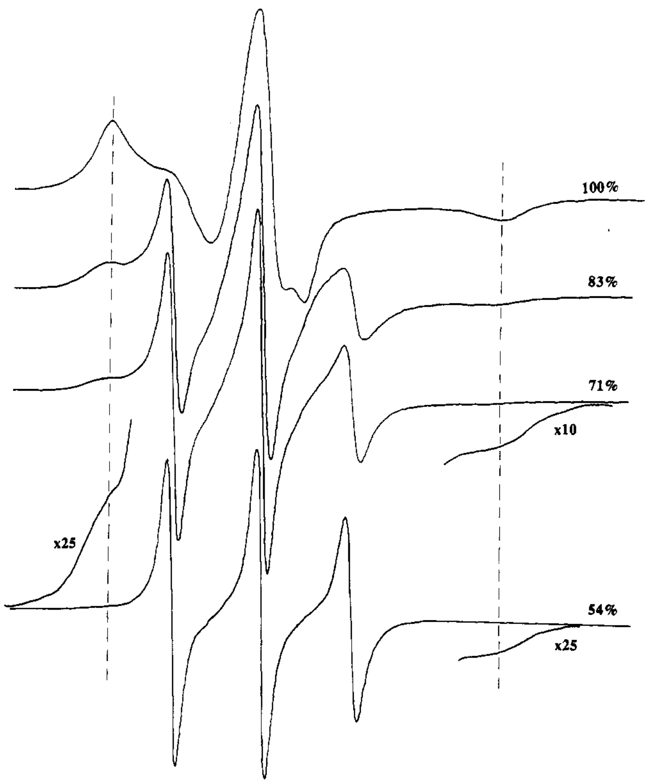

Figure 3. ESR spectra of labeled PBIC at 22 °C as a function of added CCl_4. Indicated percentage is volume percent of polymer. Dashed lines are hyperfine extrema in pure polymer.

The temperature dependence of the ESR spectra of the pure polymer is shown partially in Figure 2. At subambient temperature, not shown, a typical dilute spin, motionally slowed spectrum was observed. At −128 °C the hyperfine extrema were separated by 67 G. The line shape remained constant with the separation of the hyperfine extrema decreasing to 65 G at −25 °C and to 62 G at 22 °C. At this temperature a hint of a motionally narrowed component began to appear (Figure 2a). As the temperature was increased a rapid rise in the motion of the nitroxide was observed (Figure 2b–e).

When CCl_4 was added to the pure polymer at ambient temperature (22 °C), a motionally narrowed component to the spectrum was observed, with the hyperfine extrema of the motionally slowed component appearing to remain constant (Figure 3). At 46% solvent few motionally slowed spins were present. When benzene instead of CCl_4 was added a significant fast component to the spectrum was observed at smaller solvent composition than observed with CCl_4 (Figure 4). With only 2% by volume of benzene an easily discernible fast component was present. With 22% by volume of benzene a very small slow component was present. The superposition of a slow and a fast component to the spectrum in the presence of either solvent is interpreted as the existence of two noninterchanging populations of nitroxides, the ratio of the number of spins being composition dependent. A similar observation has been made in certain random-coil polymer–diluent pairs.[15]

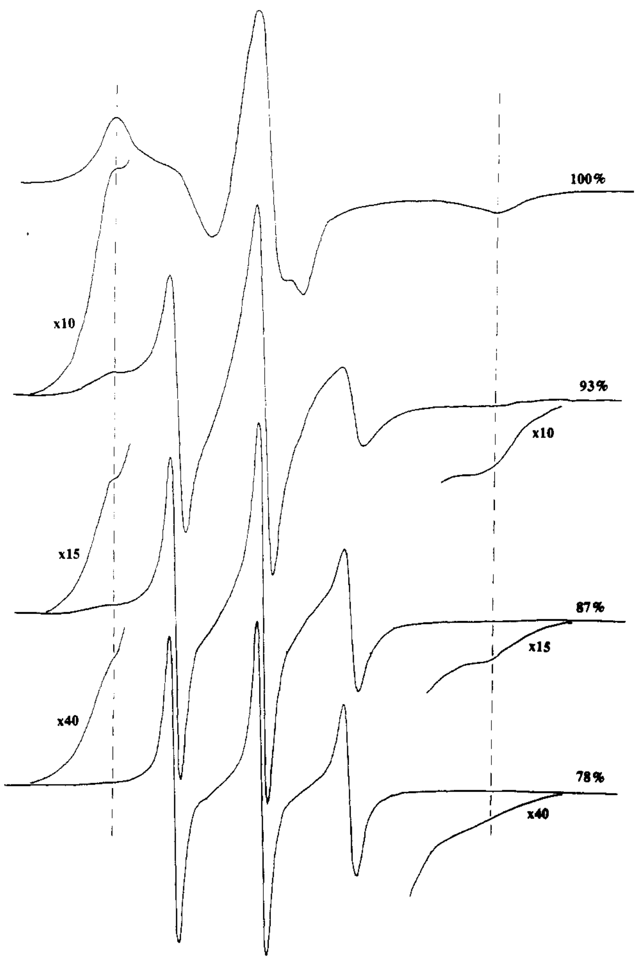

Figure 4. Same as Figure 3 except the solvent was benzene.

An alternative to studying the effect of solvent at fixed temperature is to monitor the effect of temperature at fixed composition. Typical results are shown in Figure 5, for 61% by volume of PBIC in the presence of CCl_4. As the temperature is lowered a motionally slowed component in the spectrum becomes apparent, with a difference in hyperfine extrema matching that in the bulk polymer at the same temperature. Similar results were obtained with benzene as the solvent and at different polymer compositions.

All spectra obtained for samples containing solvent can be analyzed to good approximation as a superposition of a motionally slowed and a motionally narrowed component. Using the pure polymer spectrum at the temperature of interest as the reference spectrum for the motionally slowed component, spectra were simulated using the Kivelson treatment[16] for the fast component assuming isotropic rotation. From this analysis the percent fast motion and the rotational correlation times (τ) of the fast component can be determined. The percentage of spins in the fast component is shown in Figure 6 as a function of solvent, temperature, and composition. At low polymer concentrations and higher temperatures, all spins appear motionally narrowed. The rotational correlation times at 22 °C at low PBIC concentrations are given in Figure 7. In the case of benzene, solutions cooled from 50 to 22 °C are initially metastable but ultimately phase separate, giving highly birefringent PBIC-rich dispersions. When cooled to the point where the benzene freezes and returned to 22 °C, a polymer rich, highly birefringent, polymer continuous network (gel) is formed.[17,18] The ESR spectra still show complete motional narrowing. These correlation times are also shown in Figure 7. In Figure 8 Arrhenius plots are displayed for some low-concentrations PBIC solutions. Apparent activation energies of 4–5 kcal/mol are observed, only moderately larger than the temperature dependence of the solvent viscosity.

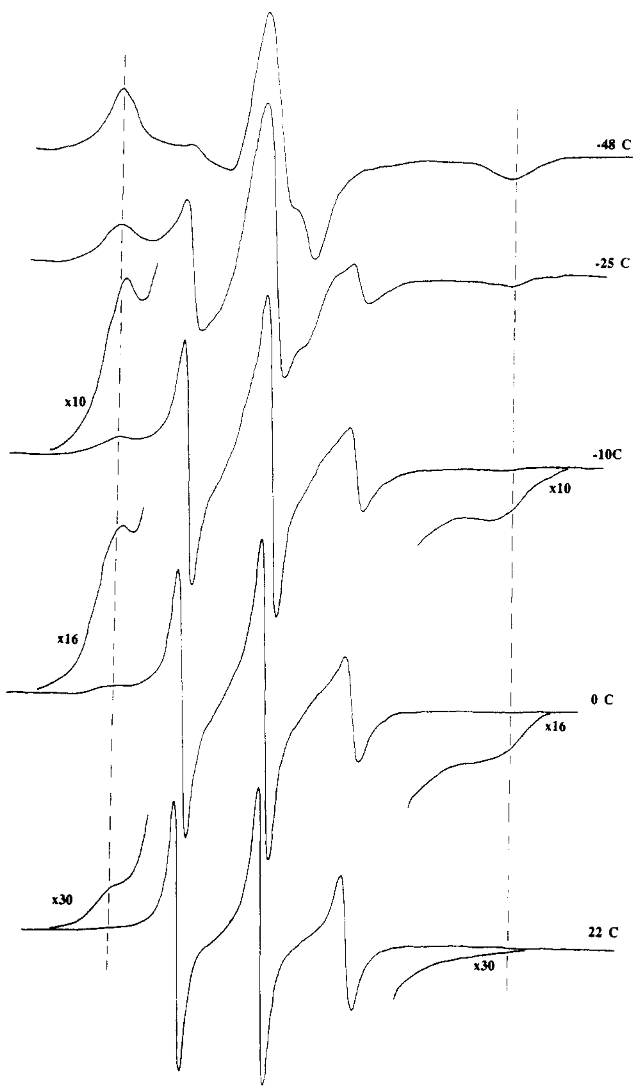

Figure 5. ESR spectra of 61% by volume of PBIC in CCl_4 as a function of temperature. Dashed lines are hyperfine extrema of pure polymer at −48 °C. The extrema separation of pure polymer are 4 G closer at 22 °C.

^1H NMR spectra at 25 °C are shown in Figure 9 for the bulk polymer and also in the presence of small amounts of vapor-sorbed diluent. At 100 °C the spectrum for the bulk polymer is still broad though individual resonances are starting to be resolved.

Discussion

The covalent incorporation of a spin label into a polyisocyanate has not been reported previously. On the basis of known reactivity of isocyanates, we propose the incorporation is as shown in Figure 1, thus making it an end-labeled polymer. Its usefulness in monitoring polymer motion, phase behavior, etc., depends on the polymer chain dynamics as well as any rotation about bonds attaching the nitroxide to the polymer. PBIC is locally stiff and in the molecular weight range studied here behaves as nearly a rigid rod in dilute solution at room temperature.[7,19–21] In solution the single bond connecting the terminal ring containing the nitroxide to the carbonyl (Figure 1) should have a low rotational barrier and experience effectively free rotation. By analogy with the-

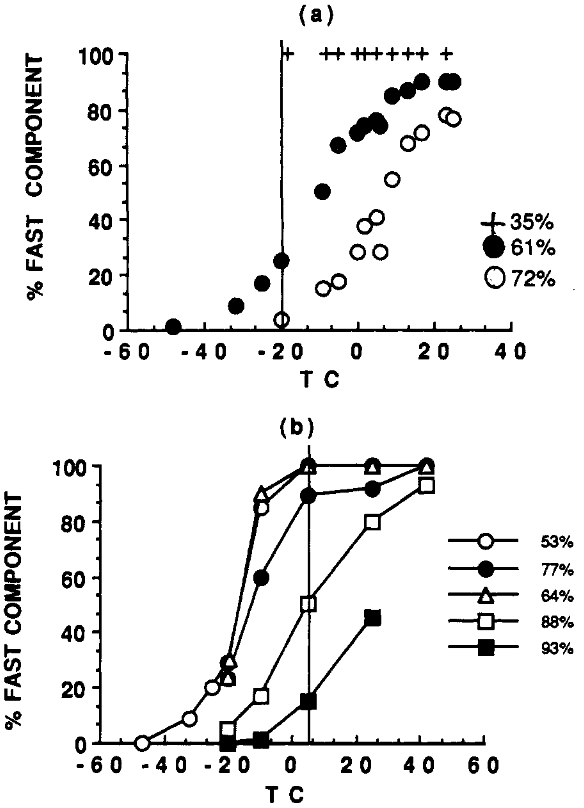

Figure 6. Percentage of spins motionally narrowed (fast component) as a function of temperature and composition (volume percent of polymer) for PBIC in CCl_4 (a) or benzene (b). Solid vertical line is the freezing point of the pure solvent.

oretical simulations and experimental observations on end-labeled poly(benzyl glutamate) (PBLG) in which there is only one bond with free rotation, a single bond rotation is not sufficient to give a motionally narrowed three-line spectrum.[3,6] However, a motionally narrowed spectrum is observed in the presence of diluent.

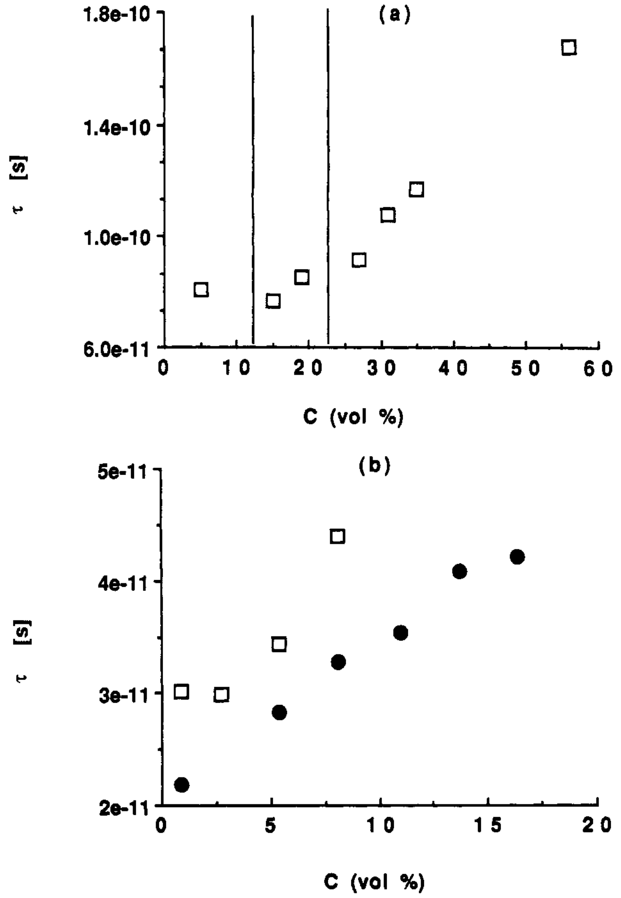

Figure 7. Rotational correlation times for PBIC–CCl_4 (a) or PBIC–benzene (b) at 22 °C as function of the concentration (volume percent of polymer). For CCl_4 the position of the phase boundaries (isotropic–biphasic, biphasic–liquid crystalline) are shown.[18] In benzene the samples were biphasic and birefringent dispersions (●) or gels (□).

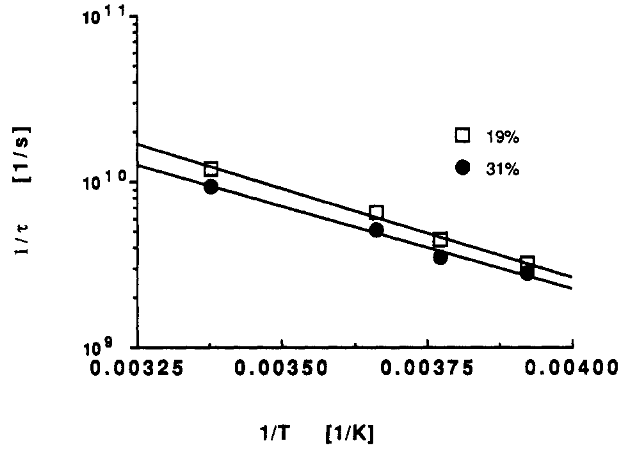

Figure 8. Arrhenius plots of the rotational correlation times of PBIC in CCl_4. Indicated concentrations are volume percent of polymer.

A motionally narrowed spectrum can also be observed in the solid state (Figure 2). From low temperatures up to room temperature a dilute spin, motionally slowed spectrum is observed, with the separation of the hyperfine extrema changing from 67 G at low temperature to 62 G at room temperature. This is consistent with increased libration or rotation about a single bond and is similar to end-labeled PBLG as well as to glassy, amorphous random-coil polymers.[15] However, as the temperature of the solid PBIC is raised above room temperature, the ESR line shape rapidly changes and by 62 °C appears to be completely motionally narrowed with a correlation time of 3×10^{-10} s. This increase appears to monitor increased motion in solid PBIC in the same temperature range as deduced from other measurements. A considerable drop in the modulus occurs in this temperature range,[17,22] and a broad maximum in tan δ occurs from 0 to 80 °C. No glass transition has been observed through this temperature region, although a weak, questionable one has been reported[23] at −15 °C. The side chains show no order at room temperature, and birefringence is reported[24,25] to be enhanced under low stress. These results, taken together, suggest that the butyl side chains, comprising about two-thirds of the volume of the polymer, may become mobile in this temperature region. Indeed, even at 25 °C the side chains have enough motion to be seen as a broad resonance on a high-resolution NMR proton spectrometer (Figure 9). At 100 °C the spectrum is still broad with a hint of some resolution among protons. For comparison the onset of mobility in the side chains of PBLG has also been observed as well as a drop in the modulus, with no observable glass transition.[26] However, side-chain mobility plus a single bond rotation does not lead to a motionally narrowed spectrum in PBLG. One must conclude that some additional motion must be present in PBIC. The magnitude of the modulus plus the breadth of the ^1H NMR resonances at 100 °C indicate that the polymer backbone is still rather stiff. Considerable effort has been put into understanding the nature of the stiffness of the isocyanate backbone[27–30] and is considered

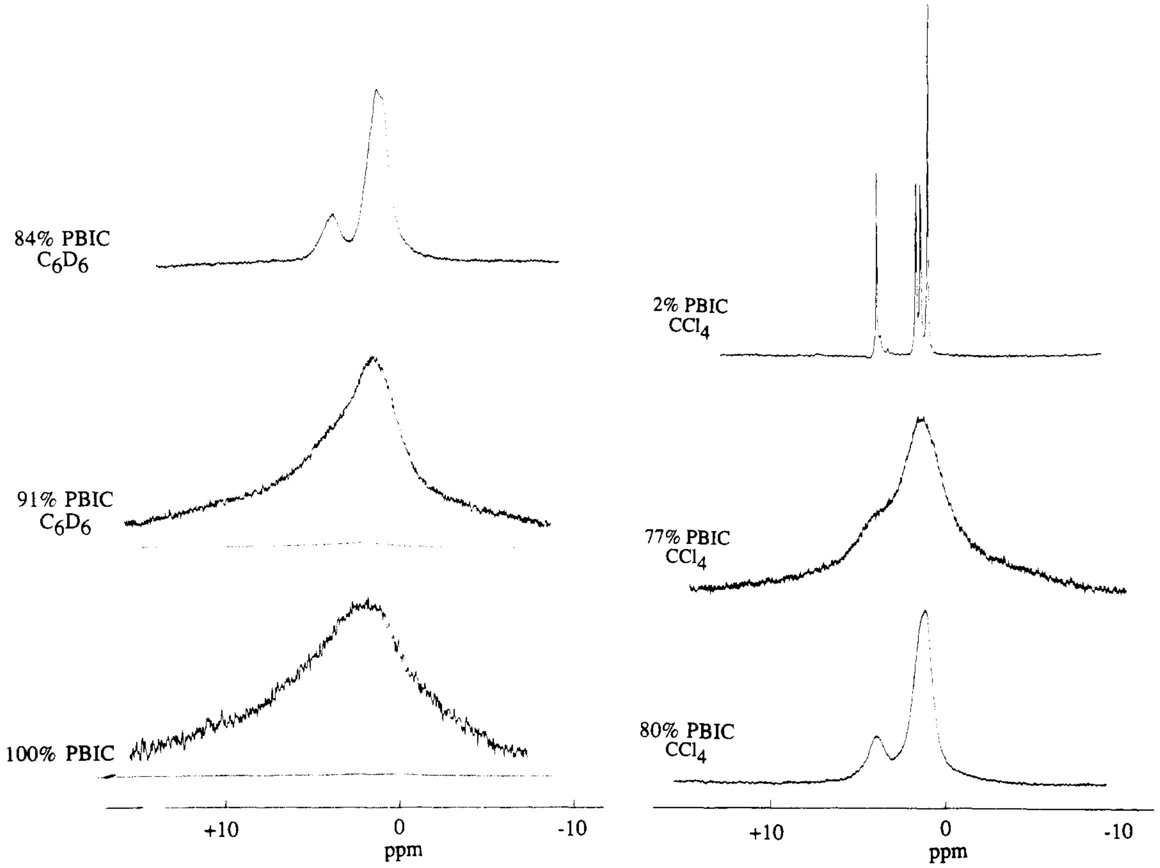

Figure 9. ^{1}H NMR spectra at 25 °C for PBIC (signal amplification not constant). The volume percents of polymer and the solvent are indicated. With pure polymer and with polymer plus 9% benzene, spectra are shown under normal high-resolution amplification and with highly enhanced amplification.

to be a combination of electronic and steric factors. The lack of a butyl group on the terminal nitrogen (Figure 1) will relieve some steric hindrance and allow additional motion to the nitroxide, provided electronic effects do not intervene. Such motion may be sufficient to give a motionally narrowed spectrum in the presence of a matrix of mobile butyl side chains. Also the chain end may exhibit more flexibility that a unit in the interior.

Turning to the addition of diluent, it is expected that the motion of the spin label should increase as diluent is added. At a molecular weight of 145 000 motion of the rodlike PBIC molecule either of or about the rod axis will have no effect on the nitroxide motion.[6] Diluent dilutes the rods and allows more freedom of motion about the end bonds. What is surprising is the ability to analyze the spectra to a good approximation as a superposition of a motionally slowed component, the same as the bulk polymer, and a motionally narrowed component. Although similar behavior has been observed in glassy, random-coil polymers with no clear explanation,[15] a plausible reason can be found here. The dry polymer before diluent addition is partially crystalline, the degree of crystallinity dependent on sample history.[22,25] The number of PBIC rods in a crystal is unknown, although the crystal size is sufficient to give relatively sharp X-ray diffraction peaks. A good solvent will preferentially go to the amorphous regions and, as more solvent is added, eventually dissolve all crystallites.[31] Crystalline regions which are not solvent penetrated would be expected to show nitroxide motion the same as in the dry polymer. In toluene crystalline regions are reported to contain no solvent.[32] Cooling a solution, as in Figure 5, can also lead to crystallite formation, which, if solvent free, would be expected to show the same nitroxide motion as dry polymer at the same temperature. The percentage of the spins in the motionally narrowed component monitors the noncrystalline component in CCl_4. When the solvent freezes (Figure 6a), this drops to zero. Supercooling of the solvent accounts for the two points with measurable fast spins below the freezing point of CCl_4. In addition to a crystalline and an isotropic phase, PBIC in CCl_4 exhibits a liquid-crystalline phase. The nitroxide correlation times shown in Figure 7 indicate that the nitroxide motion is indifferent to where the PBIC is in the isotropic or liquid-crystalline phase. This is further confirmed in Figure 8 where the Arrhenius plot for the 19% sample extends across phase boundaries. Since both phases, liquid crystal and isotropic, contain highly solvated rods, this is not surprising.

What is not so clear is the higher effectiveness of benzene over CCl_4 in the fraction of spins which are motionally narrowed, particularly as benzene appears[17,18] to be a poorer solvent for PBIC. With benzene (Figure 6b) a motionally narrowed component is evident even after the solvent is frozen. Supercooling was not observed calorimetrically below −20 °C. Inasmuch as the polymer is excluded from the benzene crystals and concentrated between them,[17] this polymer-rich phase may contain some solvent, giving motion to the nitroxide. Thus the motion observed in the presence of benzene may be more complicated to analyze than that observed in CCl_4.

The ^{1}H NMR spectra (Figure 9) indicate clearly an increase in side-chain motion upon solvent addition. In fact, the sharpness of the resonance for the methylene attached to the main-chain nitrogen in dilute polymer solutions is surprising. The lack of a measurable molecular weight dependence of the line width of this resonance indicates that rotation about the main chain does not contribute to the line width, leaving motion about the C–N bond as the only apparent source of relaxation for these methylene protons. Perhaps there is a contribution from local main-chain motion (libration), as such motion has been shown[30] to be sufficient to explain the transition from rodlike to flexible rheological behavior as a function of molecular weight.[7,32] The NMR spectra show also the effect of sample history, as seen by comparing the spectra of 20 and 22% by volume of CCl_4, samples with different thermal histories and hence different degrees of crystallinity. Thus the degree of crystallinity is affected by sample history, and the butyl mobility is affected by the amount, distribution, and nature of the solvent. The nitroxide spectra suggest that the nitroxide chain end gains mobility when surrounded by solvated polymer side chains. As the molecular weight of the nitroxide labeled polymer is in the "rigid-rod" region, local main-chain libration is the only possible contribution of main-chain motion to the nitroxide relaxation. The dynamics of PBLG is similar in that it remains nearly rodlike in many solvents but differs in that intramolecular hydrogen bonds suppress significant internal librations. Thus end-labeled high molecular weight PBLG does not exhibit a motionally narrowed ESR spectrum in dilute solution[3] as there is only one bond rotation contributing to motion. The intramolecular hydrogen bonds giving rise to a helix are intact to the end of the PBLG chain.[6] With PBIC the potential functions giving rise to main-chain stiffness are quite steep.[29,30] If, however, internal libration contributes to relaxation of the nitrogen-attached methylene protons, such libration may contribute some motion to the chain end, in addition to that contributed from motion about the two bonds special to the nitroxide attachment. Thus the motion of the chain end as monitored by the nitroxide is a complex function of main-chain dynamics and side-chain dynamics of the polymer matrix facilitated by temperature and solvent.

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Registry No. *n*-Butyl isocyanate (homopolymer), 25067-04-3; 3-carbamoyl-PROXYL, 4399-80-8.