# Nuclear magnetic resonance studies of molecular dynamics of $\beta$-propiolactone homopolymer and its block copolymer with $\beta$-butyrolactone

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Broad-line and pulse nuclear magnetic resonance (n.m.r.) investigations of $\beta$-propiolactone homopolymer and its block copolymer with $\beta$-butyrolactone are reported. Proton n.m.r. spectra and $T_1$ and $T_{1\rho}$ relaxation times studied in the temperature range from 113 K to the melting points are interpreted in terms of molecular motions and phase structure of the polymers investigated. Two regions with different mobilities in the amorphous phase of the block polymer have been found. The observed decrease of the second moment as well as the $T_1$ and $T_{1\rho}$ minima indicate the existence of molecular motions in the amorphous phase of both polymers far below their melting points. Rotation of methyl groups in the block polymer has been established.

**(Keywords: nuclear magnetic resonance; spin–lattice relaxation; poly($\beta$-propiolactone); block polymers; poly($\beta$-butyrolactone-*block*-$\beta$-propiolactone)**

## INTRODUCTION

Block polymers are considered as interesting materials because different polymer segments can be incorporated into a single polymer molecule. Anionic ring-opening polymerization presents a very convenient and flexible method for preparation of tailored 'living polymers' such as block polymers with desired architecture and properties. However, in the case of anionic polymerization of $\beta$-lactones there are limitations, since $\beta$-alkyl-substituted $\beta$-lactones were considered incapable of polymerization in the presence of anionic initiators[1]. We have recently demonstrated that alkali-metal solutions[2] are powerful initiators for anionic polymerization of $\beta$-propiolactone and its $\alpha$- and $\beta$-alkyl-substituted derivatives[3,4]. The $\beta$-butyrolactone and $\beta$-propiolactone block polymers with predictable molecular masses and compositions were obtained for the first time in this way[5]. This paper describes the use of n.m.r. spectroscopy to investigate the molecular dynamics of $\beta$-propiolactone homopolymer (PL) and 50/50 $\beta$-butyrolactone-*block*-$\beta$-propiolactone polymer (BL-PL) obtained using the above-mentioned initiator.

N.m.r. parameters in solids such as organic polymers are almost entirely determined by the magnetic dipolar interactions between the resonant nuclei. When thermal motions cause nuclei to change their positions rapidly enough, the local fields experienced by a given nucleus tend to be averaged out. Line narrowing is then observed. In addition, the time-dependent magnetic fields arising from motions of neighbouring nuclei induce transitions between the nuclear spin states and lead to thermal equilibrium between the nuclear spin system and the lattice. This process is characterized by the spin–lattice relaxation times $T_1$ and $T_{1\rho}$ in the laboroatory and rotating frames, respectively. Thus, analysis of n.m.r. spectra and nuclear magnetic relaxation behaviour may deliver valuable information about the molecular motions as well as structural heterogeneity in such materials.

## EXPERIMENTAL

### *Materials and analyses*

Poly($\beta$-propiolactone) (PL) was prepared by anionic polymerization of $\beta$-propiolactone initiated by potassium anions according to the method described previously[3]. Poly($\beta$-butyrolactone-*block*-$\beta$-propiolactone) (BL-PL) was obtained by prepolymerization of $\beta$-butyrolactone by potassium anions, followed by $\beta$-propiolactone polymerization initiated with $\beta$-butyrolactone prepolymer (BL), as described previously[5]. The 50/50 composition of the block polymer obtained was determined by proton n.m.r. spectroscopy, utilizing the intensity ratio of the signals corresponding to the prepolymer at $\delta = 1.23$ ppm (d, $CH_2$) and PL segment at $\delta = 4.24$ ppm (t, $CH_2$–O). The proton n.m.r. spectra were run in $CDCl_3$ with tetramethylsilane (TMS) as internal standard using a Varian XL-100 spectrometer.

Analysis of the $^{13}C$ n.m.r. spectrum presented in *Figure 1* indicates that the BL segment of the block polymer is atactic and contains almost the same amounts of isotactic (*m*; $\delta = 169.16$ ppm) and syndiotactic (*r*; $\delta = 169.26$ ppm)

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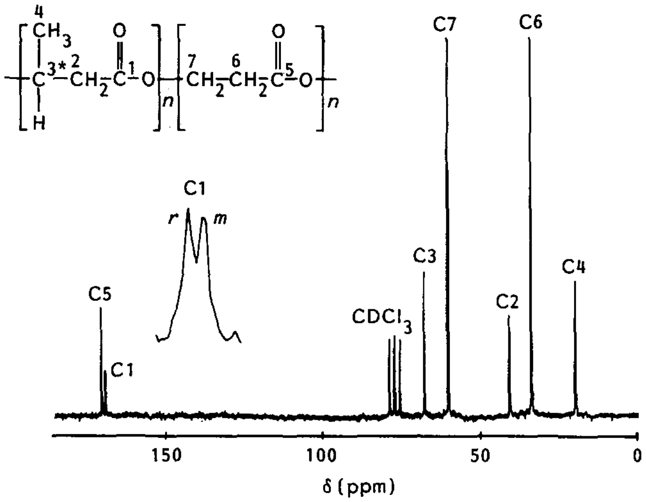

**Figure 1** $^{13}C$ n.m.r. spectrum of BL-PL block polymer. The signal of carbonyl carbon (C1) was additionally expanded with a width of plot of 150 Hz

**Table 1** Physical properties of homo- (PL) and block (BL-PL) polymers

| Polymer | $M$ (g mol$^{-1}$) | Glass transition temperature (K) | Melting temperature (K) |
|---|---|---|---|
| PL | 80 000 | 258.6 | 349.1 |
| BL-PL | 7 500 | 263.8 | 350.8 |

diads. The $^{13}C$ n.m.r. spectra were run in $CDCl_3$ using a Varian FT-80A spectrometer.

The molecular mass of PL was determined from viscosimetric measurements, as described by Shiota *et al.*[7]. The number-average molecular mass of the BL-PL block polymer was determined by the vapour-pressure osmometry (v.p.o.) technique using the Knauer vapour-pressure osmometer. The melting behaviours of the homo- and block polymers were studied by differential scanning calorimetry using a Du Pont 1090B (Thermal Analyzer) d.s.c. apparatus. Molecular masses and transition temperatures for the investigated homo- and block polymers are given in *Table 1*.

The broad-line $^1H$ n.m.r. spectra were recorded on a spectrometer driven by a marginal oscillator. The multicomponent n.m.r. spectra of the polymers were expressed as a function of the magnetic field $B$:

$$Y(B)=\sum_i A_i Y_i(B) \quad \text{with} \quad \sum_i A_i=1 \qquad (1)$$

where $Y_i(B)$ represents the elementary spectrum of the $i$th component and $A_i$ stands for the contribution of protons of the $i$th phase. Proton spin–lattice relaxation times were measured using a pulse spectrometer operating at a frequency of 25 MHz, as described by Jurga[8]. The relaxation time $T_1$ was measured by a saturation recovery method[9]. Rotating-frame data ($T_{1\rho}$) were obtained for the radiofrequency field $B_1=1.87$mT by the spin-locking method[10]. Analysis of the magnetization decay in $T_{1\rho}$ measurements was performed according to the equation:

$$M(t)=\sum_i M_i \exp(-t/T_{1\rho}^{(i)}) \quad \text{with} \quad \sum_i M_i=1 \qquad (2)$$

where $M(t)$ is the total magnetization of the sample as a function of time $t$, $M_i$ is the observed initial magnetization of the $i$th phase, $T_{1\rho}^{(i)}$ is the relaxation time of the $i$th phase, and $t$ is the duration of the spin-locking pulse.

## RESULTS

Analysis of the continuous-wave n.m.r. spectra for both polymers, recorded in the temperature range from 113 K up to the melting points, is as follows. At the lowest temperatures the spectra appear as a single broad line. Above 263 K, the spectra reveal two components, a broad and a narrow one, pointing to the presence of polymer regions of different mobility. In the case of the block polymer there are some indications of the existence of a third component which narrows to the extent of being indistinguishable well below the melting temperature. The intensity of the narrow components for both polymers increases with temperature. At temperatures above 293 K the narrow components cannot be properly recorded due to spectrometer limitations. Above the melting point only one narrow component has been observed.

The temperature dependences of the second moment for the homo- and block polymers are presented in *Figure 2*. The second moment values above 273 K refer only to the broad component. In the case of the PL homopolymer the temperature dependence of the second moment exhibits three distinct regions. From the lowest temperature up to 253 K the second moment gradually changes from 0.17 mT$^2$ to 0.15 mT$^2$ and then distinctly drops to 0.13 mT$^2$ at 293 K. At higher temperatures up to the melting point the changes of the second moment are insignificant. There are some differences in the temperature dependence of the second moment for the block polymer compared to the homopolymer. The second moment in the lowest temperature range changes from 0.15 mT$^2$ at 113 K to 0.13 mT$^2$ at 153 K, becoming almost temperature-independent in the next region up to 263 K and then decreases to the value of 0.105 mT$^2$ at 288 K. The second moment of the broad component does not change up to the melting point and is close to 0.12 mT$^2$.

Although we did not precisely analyse the free induction decay (FID) in the pulse n.m.r. experiment, it was apparent that its response reflected the temperature

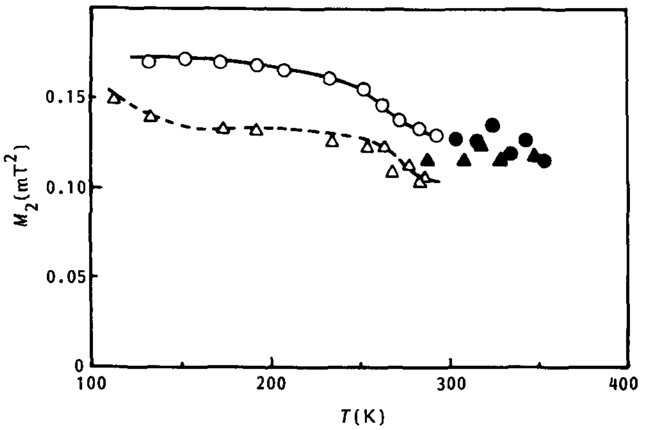

**Figure 2** Proton second moment for homo- (circles) and block (triangles) polymer *versus* temperature. Open symbols refer to the whole spectrum; the full symbols refer to the broad component only

dependence of the broad-line n.m.r. spectra. The spin–lattice relaxation time $T_1$ was exponential within experimental error whereas $T_{1\rho}$ was non-exponential in the temperature range studied. Relaxation in the homopolymer could be described by two relaxation times $T_{1\rho}^{(1)}$ and $T_{1\rho}^{(2)}$ whereas for the block polymer a third component $T_{1\rho}^{(3)}$ was additionally needed in the temperature range 270–345 K. Relaxation above the melting point is described by one $T_{1\rho}$ for the homopolymer and two $T_{1\rho}$ for the block polymer. The dependence of the FID shape on the duration of the spin-locking pulse made it possible to assign the derived relaxation times to particular regions of the polymers[11]. The temperature dependences of $T_1$ and $T_{1\rho}$ are shown in *Figures 3* and *4*. In the high-temperature range $T_1$ exhibits a minimum for both polymers. A second minimum at low temperatures is observed for the block polymer.

The observed two $T_{1\rho}$ relaxation times for the homopolymer exhibit the same temperature dependence with the formation of minima at about 313 K. The $T_{1\rho}$ temperature dependences for the block polymer are quite different, especially at high temperatures where three relaxation times are observed. Two of them ($T_{1\rho}^{(2)}$ and $T_{1\rho}^{(3)}$) reveal pronounced minima at about 300 and 323 K, whereas the minimum of $T_{1\rho}^{(1)}$ is rather shallow and occurs at a temperature close to 328 K.

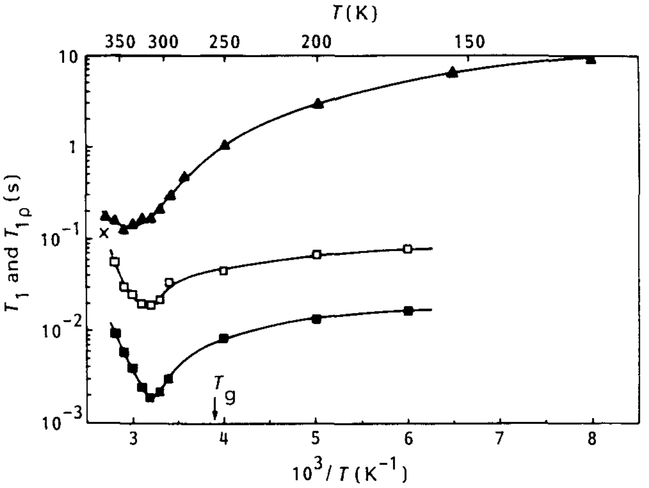

**Figure 3** Spin–lattice relaxation times $T_1$ (▲), $T_{1\rho}^{(1)}$ (□) and $T_{1\rho}^{(2)}$ (■) for homopolymer *versus* temperature ($B_1 = 1.87$ mT). The symbol × denotes the single $T_{1\rho}$ value above the melting point

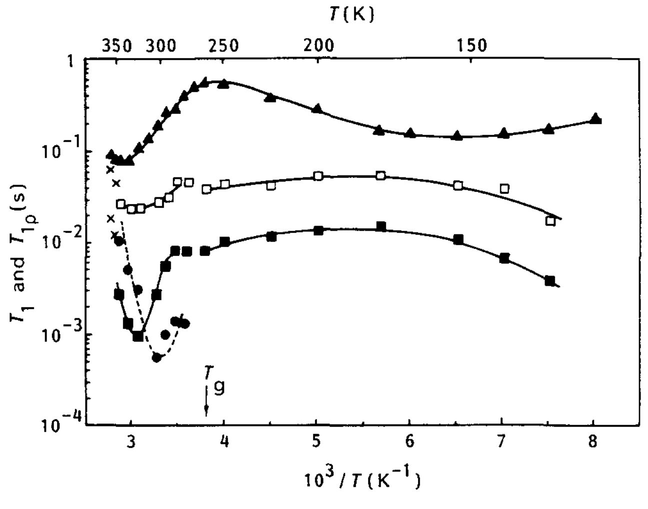

**Figure 4** Spin–lattice relaxation times $T_1$ (▲), $T_{1\rho}^{(1)}$ (□), $T_{1\rho}^{(2)}$ (■) and $T_{1\rho}^{(3)}$ (●) for block polymer *versus* temperature ($B_1 = 1.87$ mT). Symbols × denote the $T_{1\rho}$ values above the melting point

## DISCUSSION

The results presented clearly reveal structural heterogeneity and the onset of molecular motion in both systems studied. Generally, the broad component of the n.m.r. spectrum is connected with the rigid region of the polymer, while the narrow component is connected with the mobile one. Since the broad line is observed up to the melting point one can assume that it is attributable to the crystalline phase. The narrow line appears for both homo- and block polymers above 263 K. Taking into account the glass transition temperatures determined by the d.s.c. measurements (*Table 1*) it can be assumed that the narrow component is due to the motions in the amorphous phase. The third component observed for the block polymer indicates the existence of another region of amorphous phase having a different mobility.

More information about molecular motions can be derived from the second moment analysis. The theoretical second moment was calculated using Van Vleck's formula[12] as applied for a polycrystalline sample:

$$M_2 = 3.58(1/N)\sum_{i,j} r_{ij}^{-6} \qquad (3)$$

where $N$ is the number of protons per molecule and $r_{ij}$ is the proton–proton distance in angstroms. The rigid-lattice second moment for both polymers was calculated with the aid of proton positions reported in refs. 13 and 14. The value of the second moment for the isolated chain of PL is equal to 0.137 mT$^2$. Since only the $x$ and $y$ coordinates for the second chain in the unit cell were known[13], the interchain contribution to the second moment was calculated for such a chain arrangement that gave the lowest value, i.e. 0.041 mT$^2$. The fact that the experimental value is in good agreement with the theoretical one (0.178 mT$^2$) confirms the rigid structure in the low-temperature region. The modest decrease in second moment observed with temperature increase to 250 K is probably connected with some rotational oscillations of the polymer and/or to thermal expansion effects. The second moment transition observed above 253 K coincides well with the appearance of the narrow component and is probably due to molecular motion in the amorphous phase (glass transition). The observed diminishing of the second moment value of the broad component may be caused by the increase of rotational oscillations mentioned above and/or by loosening of the structure. It is worth noting that the second moment value of the broad component is close to the theoretical one calculated for an isolated chain.

Similar calculations of the second moment for block BL-PL cannot be made, since exact data for proton positions in this polymer are not available. An estimation was made assuming that the second moment represents the sum of the contributions of separated blocks. The BL contribution was calculated using the structure data[14] available and it amounts to 0.233 mT$^2$. Therefore, the theoretical value of the rigid second moment of BL-PL was calculated as 0.211 mT$^2$. This value is greater than the experimental one measured at the lowest temperature studied, indicating that some motions are already taking place. We assumed that these were due to the rotations of the methyl groups in the BL block, which started at a temperature below the lowest temperature studied. Such motional freedom of the methyl group at low temperatures was also observed in other polymers[15]. Rotation of the $CH_3$ group about its threefold axis reduced the contributions due to interactions between protons of an individual $CH_3$ group to one-quarter of the rigid-lattice value[16], while those contributions due to interactions with other protons were reduced to one-third of the rigid-lattice value[17]. Hence, the theoretical value of the second moment calculated for the case of methyl group rotation amounted to $0.13\,mT^2$ and agreed very well with the experimental one. The changes of the second moment observed at higher temperatures were similar to those observed for PL and were inerpreted in the same way.

Similar conclusions about the phase structure and molecular motion could be derived from the relaxation behaviour. In the case of the $T_{1\rho}$ temperature dependence for PL, $T_{1\rho}^{(1)}$ (long) described the relaxation in the crystalline phase and $T_{1\rho}^{(2)}$ (short) in the amorphous phase. The temperature at which the minimum of $T_{1\rho}^{(2)}$ occurred is in good agreement with the temperature of appearance of the narrow component in the spectrum and with the second moment transition.

The minimum $T_{1\rho}^{(1)}$ could indicate the existence of reorientational motions in the crystalline phase. However, the large value of the broad component's second moment in the temperature range where this minimum occurs argues against the existence of such motions. Hence it is assumed that this minimum reflects the $T_{1\rho}^{(2)}$ relaxation time changes in the amorphous phase only.

Taking into account that both $T_{1\rho}$ relaxation times depend on temperature in the same way, it seems likely that in the relaxation process the spin-diffusion mechanism is operating[18].

Comparing the magnetization amplitudes of the two components at temperatures well above $T_g$, we were able to estimate the degree of crystallinity, which amounted to 60%. It should be remembered that the magnetization intensity attributed to the crystalline phase also includes the part of the amorphous phase that acts as a sink for the crystalline phase in the relaxation process. Thus, the degree of crystallinity given here may be slightly overestimated.

In the case of the BL-PL block polymer the relaxation behaviour was more complicated. It was obvious that the $T_{1\rho}^{(1)}$ relaxation time was connected with the crystalline phase. The $T_{1\rho}^{(2)}$ and $T_{1\rho}^{(3)}$ described the relaxation processes in the amorphous phase. Since the temperatures at which the minima appeared were rather close to each other, it could be assumed that there existed two regions with a slightly different mobility in the amorphous phase, as also suggested on the basis of lineshape analysis.

The existence of two regions in the amorphous phase could be expected by considering the differences in the chemical structure of PL and BL blocks. There are no direct indications which permit definitive assignment of the two $T_{1\rho}$ relaxation times to particular blocks but some suggestions can be made. Taking into account the limitations given above, the degree of crystallinity estimated from the intensities of the magnetization components in the temperature range 280–330 K was found to be about 24%*.

According to the high-resolution $^{13}C$ n.m.r. spectra the BL chains are atactic and the crystallinity of the block polymer is assigned to the PL chains alone. Thus, the ratio of protons in the BL and PL chains of the amorphous phase is expected to be close to 4.0. The ratio of the magnetization intensities corresponding to $T_{1\rho}^{(2)}$ and $T_{1\rho}^{(3)}$ in the temperature range mentioned above is only 2.2, but considering the heterogeneity of the system and the effects of spin diffusion it is reasonable to assume that $T_{1\rho}^{(2)}$ describes the relaxation processes in the BL chains.

In the case of spin–lattice relaxation in the laboratory frame ($T_1$), spin diffusion is effective and usually one relaxation time describes the process. The high-temperature minima in both polymers result from molecular motions in the amorphous phase. The spins in the crystalline regions relax through the spins of the amorphous phase which are in good contact with the lattice. The low-temperature minimum observed for the block polymer was due to rotation of the methyl groups in the BL block. The relatively high value of $T_1$ of this minimum (140 ms) compared to the expected value of about 14 ms for an isolated methyl group is evidence for a spin-diffusion-limited relaxation[19] reflecting the fact that some protons of the PL block are quite far from the relaxation centres. The rotation of the methyl groups will also generate a $T_{1\rho}$ minimum in the lower temperature range. However, the experimental limitations allowed us only to observe decreasing $T_{1\rho}$ values with temperature.

## CONCLUSIONS

The molecular dynamics and phase structure of β-propiolactone homopolymer and its block polymer with β-butyrolactone, prepared by means of alkali-metal solutions as initiators, have been investigated.

A two-phase structure for both polymers has been observed and in the case of BL-PL polymer two regions with different mobility in the amorphous phase have been detected.

The crystallinities of the homo- and block polymers were estimated to be close to 60% and 24%, respectively. The crystallinity of the block polymer has been assigned to the PL segment only.

The observed decrease of the second moment as well as proton $T_1$ and $T_{1\rho}$ relaxation minima indicate the existence of molecular motions in amorphous phases of both polymers far below their melting points. The principal n.m.r. transition at higher temperatures were in accord with the glass transition determined by d.s.c. measurements. Rotation of methyl groups in the block polymer is observed, and spin-diffusion-limited relaxation has been suggested.

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* Measurements of $T_{1\rho}$ at $B_1 = 0.98$ mT made in the temperature range between the glass transition and the melting point for a premelted sample showed a decrease of crystallinity to about 15%. Shifts of the $T_{1\rho}^{(2)}$ and $T_{1\rho}^{(3)}$ minima to lower temperatures expected for thermally activated motions were observed

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