PII: S0032-3861(97)10229-4

Polymer Vol. 39 No. 17, pp. 4099–4105, 1998
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0032-3861/98/$19.00+0.00

Microphase structures of polymers containing structural heterogeneity as probed by n.m.r. spin-lattice relaxation analysis

Seung-Yeop Kwak* and Sang Yong Kim
Department of Fiber and Polymer Science, Seoul National University, San 56-1, Shinlim-Dong, Kwanak-Ku, Seoul 151-742, South Korea
(Received 27 September 1996; revised 27 February 1997; accepted 21 October 1997)

Structural heterogeneities in commercial polymers such as poly(vinyl chloride) (PVC), segmented copoly(ether-ester) block copolymer, and nitrile rubber were analyzed by cross-polarisation/magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. The results from rotating and laboratory frame spin-lattice ($T_{1\rho}$ and T_1) relaxation behaviour provided a clear insight into the structural heterogeneity. Monitoring of the $T_{1\rho}$ or T_1 magnetisation decay behaviour and determining of the corresponding relaxation times for the specific carbons of the three polymers allowed a further precise analysis of the microphases and an estimation of quantitative information pertaining to the structural heterogeneity. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: structural microheterogeneity; CP/MAS ^{13}C n.m.r. spectroscopy; spin-lattice relaxation)

INTRODUCTION

Poly(vinyl chloride) (PVC) and segmented copoly(ether-ester) block copolymer are widely used commercial polymers. Two polymers have common features[1–6]: (i) they contain a physically heterogeneous structure at a molecular level, which is distributed throughout the amorphous phase; (ii) the structural heterogeneity is important in governing the solid-state properties, acting as thermally reversible physical cross-links; and (iii) the structural heterogeneity not only gives rise to an elasto-plastic nature but also exerts high modulus and strength in the polymers. Nitrile rubber has been successfully used in oil field applications as down hole packers, blow-out preventers, and stripper elements[7,8]. Uncrosslinked nitrile rubber is usually considered as entangled random coils of polymer chains. However, even in such a noncrystallisable amorphous gum rubber, there may exist a substantial fraction of structural heterogeneity on the molecular or microdomain level.

The microscopic structure and morphology of these polymers have been studied extensively. PVC consists of basic particles of about 10 nm, called microdomains, which aggregate to form subsequent hierarchical particles, namely domain (~0.1 μm), primary particle (~1 μm), agglomerate (~10 μm), and finally grain (~150 μm), covered by a skin[9–11]. The microcrystallites of short (5–12 monomer units) syndiotactic sequences of the chains internally connect the microdomain, regarded as the structural heterogeneity (*Figure 1a*). Copoly(ether-ester) exhibits two-phase–phase morphology composed of microseparated crystalline domains of hard segments and amorphous phase of soft segments, in which some of the vitrified hard-segment units reside (*Figure 1b*)[10–12]. The structural heterogeneity of this polymer may involve both crystalline domains and vitrified units of hard segments. Commercial nitrile rubber is prepared by the emulsion polymerisation of butadiene and acrylonitrile monomers[15]; the acrylonitrile content varies from 15 to 50%. The two monomers have quite different reactivity ratios and the acrylonitrile tends to be consumed fast. It is therefore necessary to incorporate acrylonitrile in stages during the polymerisation in order to obtain a reasonably uniform product. However, when the polymerisation is carried to a high conversion, the formation of the structurally heterogeneous phase of the butadiene blocks is often suspected to be due to the difference in the butadiene and acrylonitrile ratio; to date, there is no information on the nature of the heterogeneity in this polymer. Despite the well-defined morphology and structure of these polymers, the amount and the size of the structural heterogeneity in them have been a matter of controversy and their details are still an open question.

The objective of this study is to probe the structural heterogeneity on the molecular level and to estimate its amount (as well as its size) in 'as-received' commercial PVC, copoly(ether-ester), and nitrile rubber. Solid-state ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy capable of cross-polarisation/magic angle spinning (CP/MAS) is employed as a probe for the structural heterogeneity.

Because the structural heterogeneity of these polymers has a broad distribution in concentration, is small, and has relatively low crystallinity and wide melting range (especially for PVC[16]), it is rather difficult to clearly observe its presence with the conventional analytical techniques, such as differential scanning calorimetry and dynamic mechanical analysis.

In the CP/MAS ^{13}C n.m.r., the carbon magnetisation during the delay decays exponentially in polarisation of their proton reservoirs, allowing proton spin-lattice relaxation. The carbon magnetisation associated with different

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* To whom correspondence should be addressed

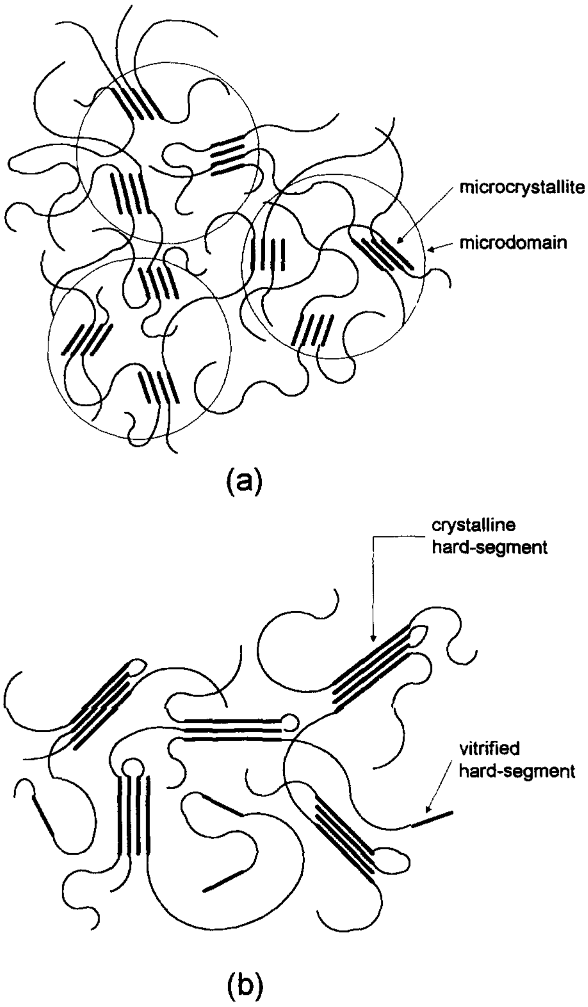

Figure 1 Schematic illustration of microstructure of poly(vinyl chloride) (a) and copoly(ether-ester) (b)

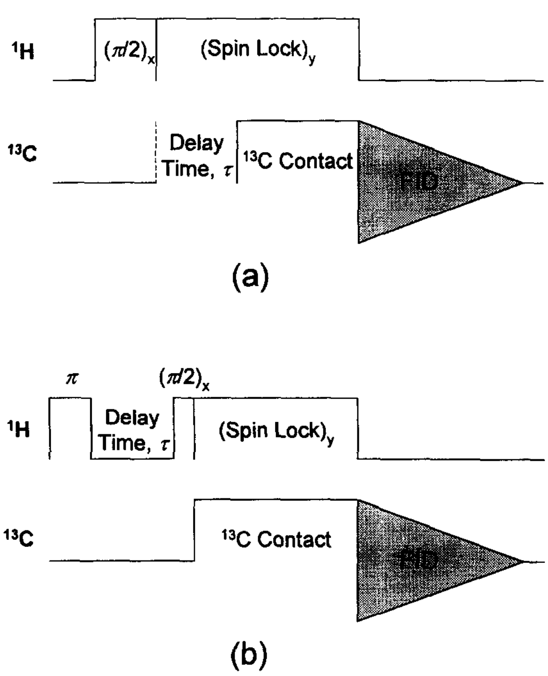

Figure 2 Cross-polarization (CP) pulse sequence to measure proton spin-lattice relaxation times under Hartmann-Hahn match: (a) $T_{1\rho}$ and (b) T_1

types of phases (homogeneous or structurally heterogeneous) may result in the double-component exponential decay corresponding to the individual phases. Numerical analysis on the respective fractions of the exponential decay permits a quantitative determination of the amount of homogeneous and the structurally heterogeneous phases. The proton spinlattice relaxation times either in the rotating frame, $T_{1\rho}$, or in the Zeeman frame, T_1, pertinent to the respective homogeneous and structurally heterogeneous phases are determined from the slopes of the semi-logarithmic plot of the magnetisation intensity, $M(\tau)$, against delay time, τ. Then, information on the spatially averaged maximum dimension of the structurally heterogeneous phase can be estimated by an approximate approach based on the spin diffusion phenomenon[17]. Depending on the relaxation time being used (i.e. $T_{1\rho}$ or T_1), the structural heterogeneity can be characterised at two size levels having a difference of *ca.* 1 order of magnitude.

EXPERIMENTAL

Commercial-grade PVC resin used was LS 050 (M_n = 30 000) supplied by LG Chem. It is used especially because its high heat stability and chemical resistance are usually required. Copoly(ether-ester), Kopel KP3340, was obtained in pellet form from Kolon Co. It comprises hard polyester segments, of polytetramethylene terephthalate, creating physical cross-links upon crystallisation. The hard segments and their noncrystalline parts are dispersed in the amorphous matrix consisting of soft polyether segments, i.e. poly(tetramethyl ether) glycol terephthalate (with a number-average molecular weight of 1000). The distribution of the blocks is assumed to be random[3]. Nitrile rubber, Hycar VT 380 (Zeon Chemical), contains 30% acrylonitrile. It has a single glass transition temperature of $-$ 28°C.

The CP/MAS ^{13}C n.m.r. spectra were recorded with either a Bruker MSL-200 spectrometer (200 MHz for ^{1}H) or a Chemagnetic CMX-300 spectrometer (300 MHz for ^{1}H), both equipped with a magic angle spinning probe. In the CP/MAS ^{13}C n.m.r., the naturally rare ^{13}C spins are polarised through the dipolar coupling with the abundant ^{1}H spins and the magnetisation of the ^{1}H is transferred to the ^{13}C. This brings about significant enhancement of ^{13}C signal intensity and reduction in data acquisition time[18]. Moreover, the MAS contributes to the removal of the heteronuclear dipole–dipole interactions and the chemical shift anisotropy, thereby narrowing the line widths of the spectrum; the resonance of carbons attached to the different nuclear environments can be resolved[19]. Polymer samples in the form of powder (PVC), chopped pellets (copoly(ether-ester)), or cut pieces of approximately 1 × 1 mm^2 squares (nitrile rubber) were packed in rotors and spun at a rate of about 3.5–4 kHz. The ^{1}H 90° pulse widths were 4.5 μs for MSL-200 and 4.25 μs for CMX-300, respectively. $T_{1\rho}$ spin-lattice relaxation times were measured by using a ^{1}H spin-lock τ-pulse sequence followed by the cross-polarisation (CP), as shown in *Figure 2a*. T_1 spin-lattice relaxation times were measured by inversion-recovery pulse sequence (π–τ–$\pi/2$) prior to CP (*Figure 2b*). The cross-polarisation Hartmann-Hahn contact time of 1 ms for both probes was taken.

RESULTS AND DISCUSSION

Figure 3 is a series of the CP/MAS ^{13}C n.m.r. spectra (called stack spectra) of PVC, which was obtained from introducing various delay times, τ, between the 90° pulse and the CP in

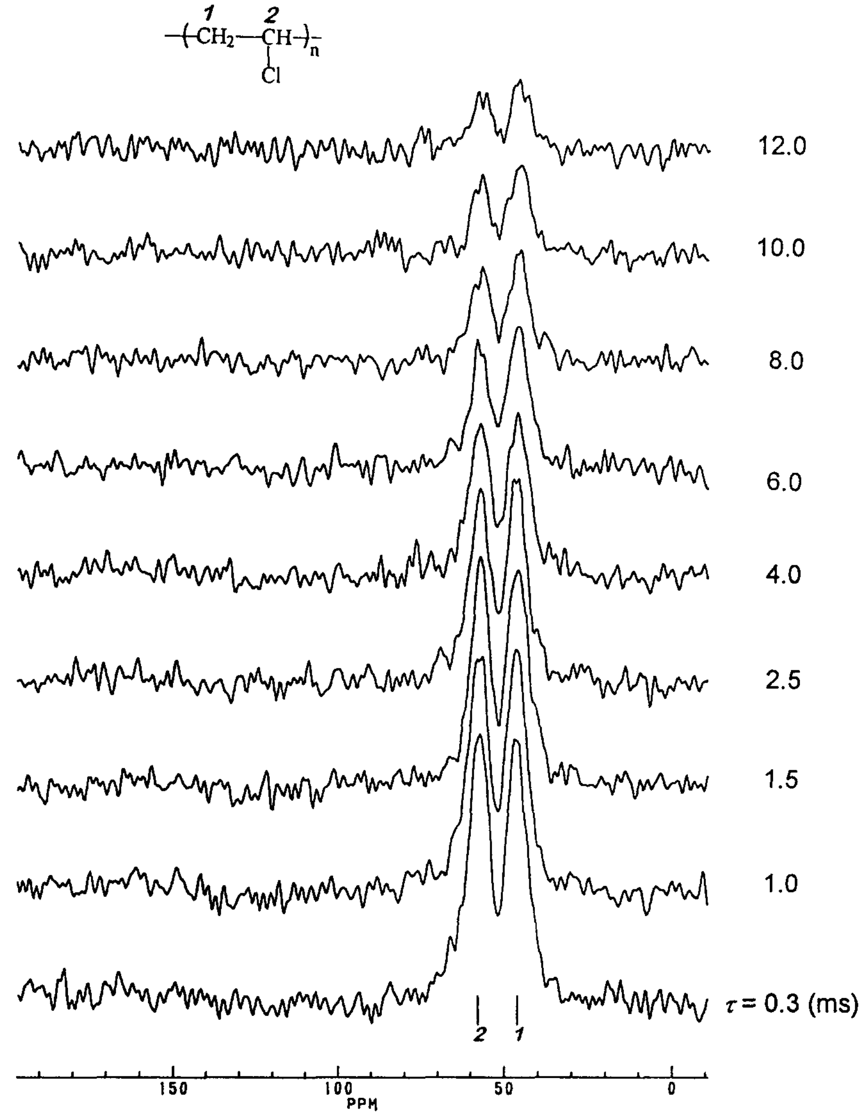

Figure 3 CP/MAS ^{13}C n.m.r. stack spectra of poly(vinyl chloride) to determine proton $T_{1\rho}$ spin-lattice relaxation times

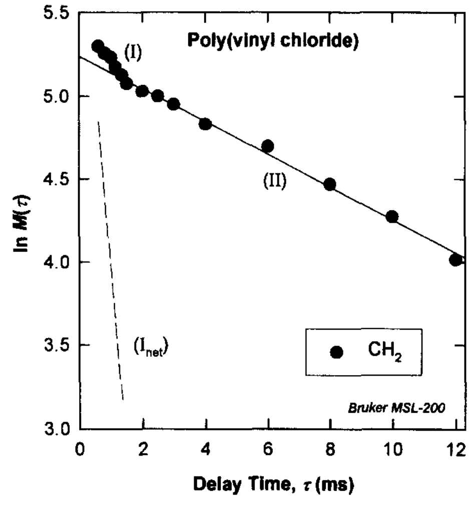

Figure 4 Logarithmic plot of $T_{1\rho}$ exponential decay *versus* various delay times for poly(vinyl chloride)

the $T_{1\rho}$ pulse sequence shown in *Figure 2*. The two peaks at 46 (peak 1) and at 57 ppm (peak 2) are assigned to methylene (CH_2) and methine (CH) carbons, respectively. The $T_{1\rho}$ relaxation process follows such an exponential function:

$$M(\tau) = M_0 \exp(-\tau/T_{1\rho}) \quad (1)$$

where M_0 is the initial height of the free induction decay when the radiofrequency field is switched off. Thus, monitoring of the decay of magnetisation intensities, $M(\tau)$, permits an analysis of the $T_{1\rho}$ spin-lattice relaxation behaviour and determination of the $T_{1\rho}$ relaxation times. The plot of logarithm of $M(\tau)$ for CH_2 carbons against delay times, τ, is represented in *Figure 4*. A double-component $T_{1\rho}$ relaxation behaviour is clearly observed as indicated by the slope change. This indicates that spin diffusion within the proton nuclear spin system of the homopolymer is not capable of averaging out the $T_{1\rho}$ relaxation, implying a presence of a structurally heterogeneous phase with different mobility of molecular chains. The $T_{1\rho}$ relaxation of the two components, (I) and (II), can be described by

$$M(\tau) = M_{0,\mathrm{I}} \exp(-\tau/T_{1\rho,\mathrm{I}}) + M_{0,\mathrm{II}} \exp(-\tau/T_{1\rho,\mathrm{II}}) \quad (2)$$

It should be noted that the relaxation decay of component (I) involves contribution from that of component (II)[20]. Therefore, the decay portion contributed by component (II) must be subtracted from the decay of component (I) in order to

Table 1 Results of proton $T_{1\rho}$ measurements for poly(vinyl chloride), copoly(ether-ester) and nitrile rubber

	Homogeneous phase			Structurally heterogeneous phase		
Poly(vinyl chloride)	$T_{1\rho,\mathrm{I}}$	$M_{\mathrm{o,I}}$	Fraction (%)	$T_{1\rho,\mathrm{II}}$	$M_{\mathrm{o,II}}$	Fraction (%)
CH_2	0.45	487.84	72	10.01	188.67	28
Copoly(ether-ester)	$T_{1\rho,\mathrm{I}}$	$M_{\mathrm{o,I}}$	Fraction (%)	$T_{1\rho,\mathrm{II}}$	$M_{\mathrm{o,II}}$	Fraction (%)
CH_2	1.01	315.77	69	6.33	145.33	31
Non-protonated aromatic carbons			$T_{1\rho} = 1.93$		$M_{\mathrm{o}} = 64.72$	
C=O			$T_{1\rho} = 1.96$		$M_{\mathrm{o}} = 86.49$	
Nitrile rubber	$T_{1\rho,\mathrm{II}}$	$M_{\mathrm{o,II}}$	Fraction (%)	$T_{1\rho,\mathrm{I}}$	$M_{\mathrm{o,I}}$	Fraction (%)
CH_2	1.68	5.45	73	0.50	2.03	27
CN			$T_{1\rho} = 1.72$		$M_{\mathrm{o}} = 4.35$	

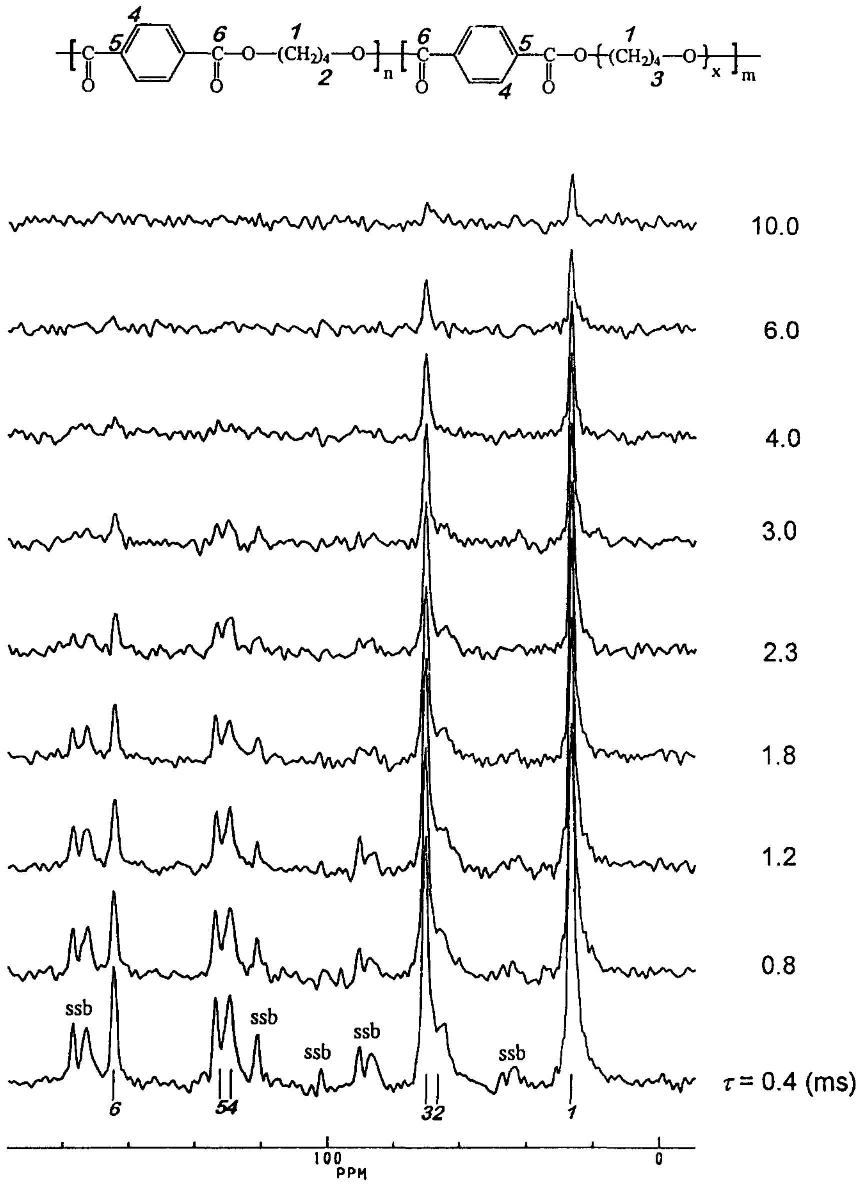

Figure 5 CP/MAS ^{13}C n.m.r. stack spectra of copoly(ether-ester) to determine proton $T_{1\rho}$ spin-lattice relaxation times. The spinning side band is labelled ssb

obtain the net relaxation of component (I), i.e. (I_{net}). The $T_{1\rho}$ values and fractions corresponding to components (I) and (II) are determined from their individual slopes and relative ratio between $M_{\mathrm{o,I}}$ and $M_{\mathrm{o,II}}$, respectively. The resulting relaxation parameters are summarised in *Table 1*. In general, the magnetisation of the relatively more mobile (amorphous) phase may have a shorter $T_{1\rho}$ than that of the relatively more rigid (crystalline) phase[21]; however, it is not always true[20]. Therefore, the assignment of components (I) and (II) to the different phases must be made with reference to the various known facts about the given polymer. For the case of PVC, the assignment was made by considering that the fraction of the microcrystallites observed by X-ray scattering is usually 8–10% for the general purpose commercial PVC, and sometimes up to *ca.* 30%, depending on the polymerisation conditions[2,22]. Component (I) belongs to the mobile amorphous (i.e. homogeneous) phase and component (II) to the rigid microcrystalline (i.e. structurally heterogeneous) phase. From the relative fraction of $M_{\mathrm{o,II}}$, the microcrystalline portion in this PVC is found to be *ca.*

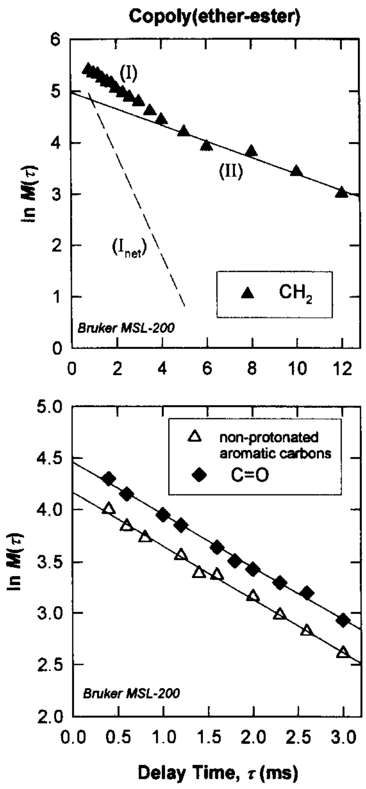

Figure 6 Logarithmic plots of $T_{1\rho}$ exponential decay *versus* various delay times for copoly(ether-ester)

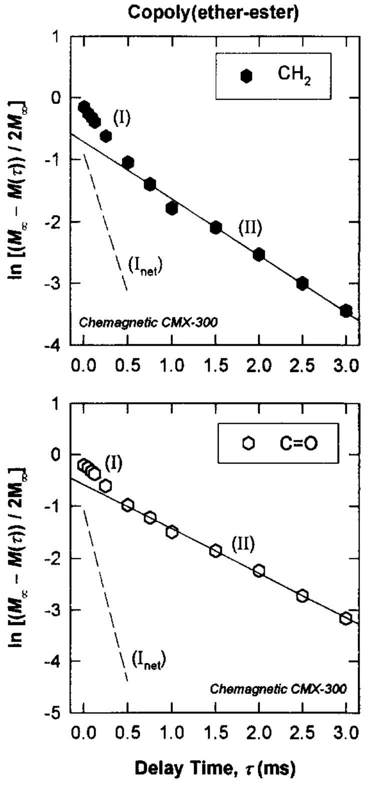

Figure 7 Logarithmic plots of T_1 exponential decay *versus* various delay times for copoly(ether-ester)

28%. The relatively high microcrystalline fraction of this grade compared to that of the general purpose grades indicates the high heat stability and chemical resistance, as the manufacture suggests. Relaxation parameters for the CH carbons, although not shown here, were identical to those in *Table 1*, thus indicating a strong dipolar coupling between protons via spin diffusion.

Figure 5 represents the ^{13}C $T_{1\rho}$ stack spectra of copoly(ether-ester) and the peak assignments, as indicated in the figure, have been made by referencing the previously published literature[23,24]. The exponential decay behaviour of the central CH_2 carbon peak heights (*Figure 6*) clearly demonstrates contributions of two quite distinct components with $T_{1\rho}$ values of 1.01 ms for (I) and 6.33 ms for (II) (see *Table 1*). This behaviour indicates that there must be a structurally separated phase interfering with an efficient spin diffusion to average out the $T_{1\rho}$ values. Component (I) is assigned to a more mobile and component (II) to a rigid phase. The relaxation behaviour and $T_{1\rho}$ values of both nonprotonated aromatic and carbonyl (C=O) carbons are identical (see *Table 1*), considering an experimental uncertainty. This trend suggests that the intersegment proton–proton dipolar interactions are strong enough for an effective communication between the proton spin system and the lattice, and thus the spin diffusion reflects an average relaxation time on the time scale characterised by $T_{1\rho}$.

Figure 7 shows plots of the ^{13}C magnetisation intensities of CH_2 and C=O carbons against delay times to measure proton T_1 values for copoly(ether-ester). Because the magnetisation intensity, assuming a perfect π pulse in *Figure 2b*, decays exponentially with a time constant equal to T_1,

$$M(\tau) = M_\infty[1 - 2\exp(-\tau/T_1)] \tag{3}$$

a plot of $\ln[M_\infty - M(\tau))/2M_\infty]$ *versus* τ yields T_1 relaxation times; M_∞ is the intensity of the signal at $\tau \geq 5T_1$. Two-component T_1 magnetisation decay can be described by:

$$M(\tau) = M_{\infty,\mathrm{I}}[1 - 2\exp(-\tau/T_{1,\mathrm{I}})] + M_{\infty,\mathrm{II}}[1 - 2\exp(-\tau/T_{1,\mathrm{II}})] \tag{4}$$

The plots of $\ln[(M_\infty - M(\tau))/2M_\infty]$ *versus* τ for both CH_2 and C=O carbons resolve into two components, and the net magnetisation is extracted in a manner similar to that of $T_{1\rho}$ case. T_1 relaxation times derived from the slopes of individual straight lines are determined to be almost identical, as listed in *Table 2*. Component (II) with longer T_1 is identified as a more mobile phase (i.e. polyether soft segments), and component (I) with shorter T_1 as a more rigid phase (i.e. polyester hard segment). It is understood that the rate of spin diffusion in the T_1 relaxation is influenced by a longer range of spatial proximity than that in the $T_{1\rho}$ relaxation, so that the state of solid phase is assessed on a larger scale by roughly one order of magnitude[25,26]. Considering that (i) the lamellar crystalline region of the hard segments seems to exceed the range for the $T_{1\rho}$ probe to be effective, and (ii) isolated phases consisting of uncrystallisable hard-segment units reside in the elastomeric phase,[12–14] components (I) of T_1 and (II) of $T_{1\rho}$ are pertinent to the crystalline hard phase and the isolated phase, respectively. From the fraction of the T_1 component (I), the crystallinity of copoly(ether-ester) is determined to be 41–45%. From the fraction of the $T_{1\rho}$ component (II), it is found that a substantial fraction (*ca.* 33%) of the isolated hard segments is present in this copolymer.

Figure 8 shows the ^{13}C $T_{1\rho}$ stack spectra of nitrile rubber, in which two peaks at 33 and 130 ppm arise from the CH_2 and CN carbons, respectively. The resulting relaxation behaviour, after monitoring the exponential decay of peak

Table 2 Results of proton T_1 measurements for copoly(ether-ester)

	Homogeneous phase			Structurally heterogeneous phase		
	$T_{1,\mathrm{II}}$	$M_{\infty,\mathrm{II}}$	Fraction (%)	$T_{1,\mathrm{I}}$	$M_{\infty,\mathrm{I}}$	Fraction (%)
CH_2	1.11	0.49	55	0.22	0.41	45
C=O	1.17	0.53	59	0.20	0.37	41

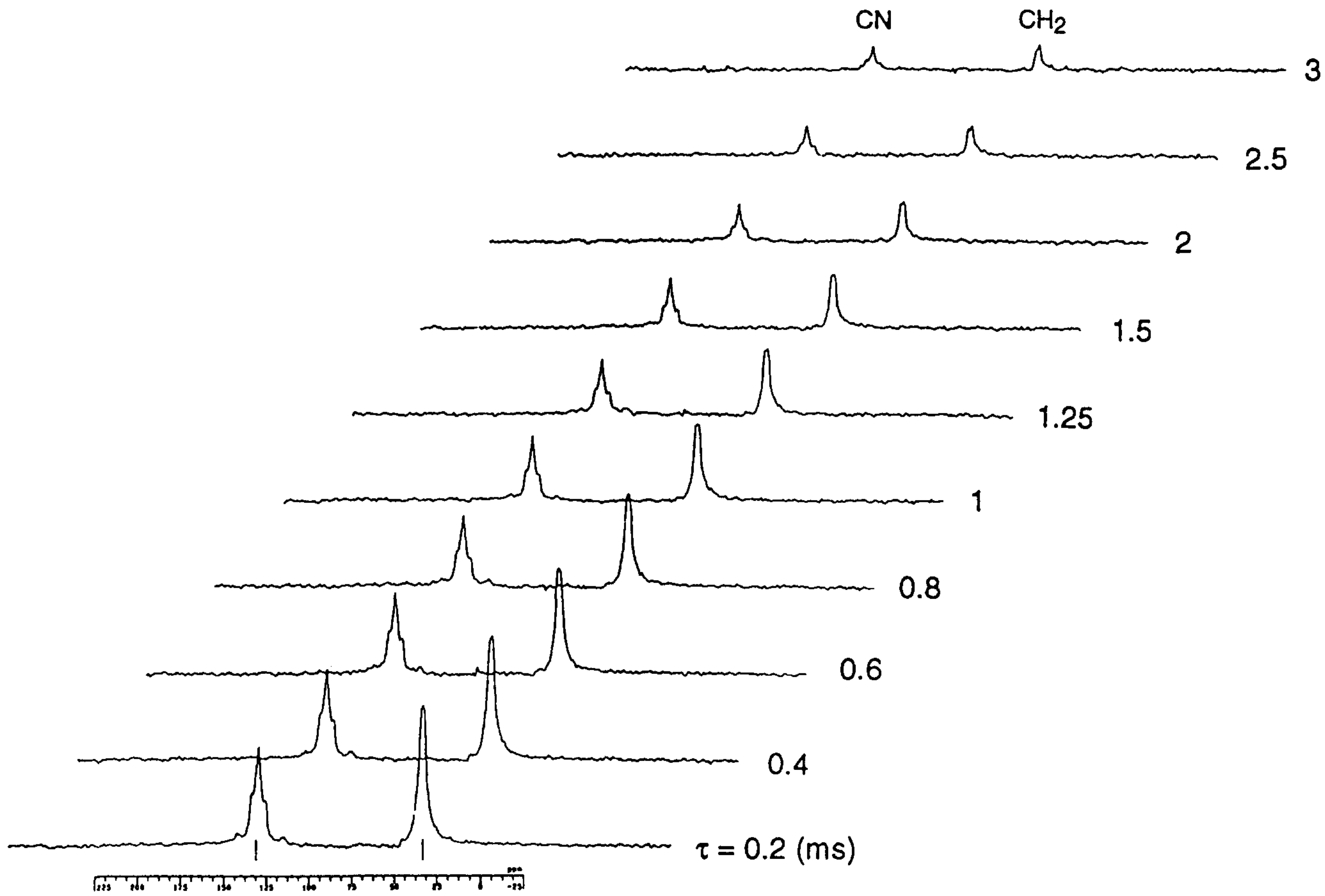

Figure 8 CP/MAS ^{13}C n.m.r. stack spectra of nitrile rubber to determine proton $T_{1\rho}$ spin-lattice relaxation times

intensities of the specific carbons (CH_2 and CN), is given in *Figure 9*. As seen in *Table 1*, separate decay components and the resulting two different $T_{1\rho}$ relaxation times (0.50 ms for component (I) and 1.68 ms for component (II)) are observed for the CH_2 carbons. For the case of nitrile rubber, component (I) is assigned to the structurally heterogeneous phase, and component (II) is contributed from the homogeneous phase. The former is conjectured to be butadiene blocks which have not been reacted with acrylonitrile during polymerisation. Quantitative determination of relative fractions of both phases indicates that a considerable amount (*ca.* 27%) of butadiene blocks exists structurally separated in nitrile rubber. In contrast, a single $T_{1\rho}$ value (1.72 ms) is found for the CN carbons, which is almost identical to that of component (II) of CH_2 carbons. The identical value reveals a tight coupling in the proton spin system, thus a homogeneous phase on the scale covered by the spin diffusion. From this value, it is possible to estimate the upper limit to the structurally heterogeneous phase through the application of the following equation[26,28,29]:

$$\langle r \rangle = (6DT)^{1/2} \qquad (5)$$

The $\langle r \rangle$ is the average diffusive path length for an effective spin diffusion. D is the spin diffusion coefficient determined by the average proton-to-proton distance and the strength of the dipolar interaction; it has typically a value of about $10^{-12}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. T is the characteristic time over which the spin diffusion proceeds, i.e. $T_{1\rho}$. Thus, the maximum scale of the structurally heterogeneous phase (butadiene blocks) is approximately estimated to be ~10 Å, which is presumably a concentration fluctuation rather than distinct domains.

CONCLUSIONS

On the basis of either bi-exponential $T_{1\rho}$ or T_1 spin-lattice relaxation behaviours and intrinsic relaxation parameter measurements for the CH_2 carbons of PVC, copoly(ether-ester), and nitrile rubber, the spatially distributed fractions of the structural heterogeneity were found to be *ca.* 28, 45, and 27%, respectively. The $T_{1\rho}$ relaxation of the CH_2 carbons of copoly(ether-ester) permitted an analysis pertinent to the isolated uncrystallisable hard segments and confirmed their existence with a substantial amount. In the case of nitrile rubber, the identical $T_{1\rho}$ relaxation times of CH_2 and CN carbons revealed that the butadiene–acrylonitrile blocks formed the homogeneous phase. From the two different $T_{1\rho}$ values of CH_2 carbons, the butadiene

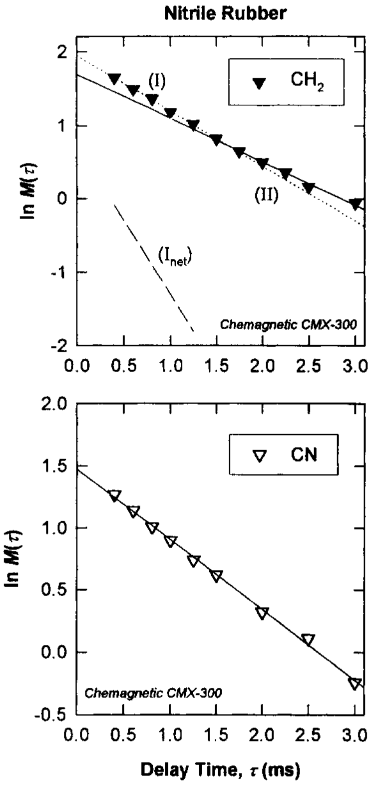

Figure 9 Logarithmic plots of $T_{1\rho}$ exponential decay *versus* various delay times for nitrile rubber

blocks which might have not participated in the polymerisation reaction were regarded as the structural heterogeneity, and phase separated from the homogenous butadiene–acrylonitrile blocks. The maximum scale of the heterogeneous butadiene blocks was estimated to be approximately 10 Å, possibly a concentration fluctuation.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the stimulating and valuable discussion with Professor N. Nakajima at Institute of Polymer Engineering, The University of Akron.

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