

N.M.R. INVESTIGATION OF INTERPHASES AND MICROPHASE COMPOSITION IN (METHYLMETHACRYLATE)-*B*-(*N*-BUTYLACRYLATE) BLOCK COPOLYMERS

Roelof Soltani^a, Françoise Lauprêtre^a, Lucien Monnerie^a and P.Teyssié^b

^a*Laboratoire de Physico-Chimie Structurale et Macromoléculaire associé au C.N.R.S.,
E.S.P.C.I., 10 rue Vauquelin, 75231 Paris, Cedex 05, France*

^b*Centre d'Etude et de Recherche sur les Macromolécules, Université de Liège, Sart-Tilman, 4000 Liège,
Belgique*

¹H nuclear magnetic resonance (n.m.r.) relaxation data, determined *via* either wide-line ¹H n.m.r. or high-resolution solid-state ¹³C n.m.r., were used to analyse the existence and extent of interphasic regions in (methylmethacrylate)-*b*-(*n*-butylacrylate) block copolymers. Results thus obtained have shown that the as-obtained copolymers are not at thermodynamic equilibrium. Some *n*-butylacrylate units are trapped in the hard microphase, whereas some methylmethacrylate units are trapped in the soft microphase. On annealing the samples at temperatures far above the glass transition temperature of the hard microphase, both blocks are allowed to diffuse and phase separate, so that thermodynamic equilibrium can be reached. Differences in the diffusion efficiency have been observed as a function of the hard block length and number of blocks. © 1998 Elsevier Science Ltd. All rights reserved.

KEYWORDS: ¹H n.m.r.; ¹³C n.m.r.; relaxation

The bulk organization of block copolymers based on methylmethacrylate (MMA) units and *n*-butylacrylate (BuA) units cannot be easily investigated by most classical techniques. Their morphology cannot be determined by using transmission electron microscopy (TEM) experiments, due to the lack of marked differences in the chemical structure of the two monomers. Differential scanning calorimetry (d.s.c.) and dynamical mechanical analysis (DMA) clearly demonstrate the existence of both hard and soft microphases. However, the presence of an eventual interphase is totally hidden by the broad β transition of the MMA units, which lies in the temperature range between the glass transition temperatures of the two blocks where the manifestation of interphases is expected¹.

On the other hand, ¹H nuclear magnetic resonance (n.m.r.) experiments may be considered an interesting tool for investigating such systems. Indeed, since, at room temperature, the hard and soft microphases are at temperatures well below and above their glass transition temperature, respectively, the hard block should exhibit a fast solidlike free induction decay whereas the soft block should yield a much slower free induction decay, typical of a rubbery behaviour. Besides, the contrast between the two microphases should be large enough to eventually detect the

presence of a phase with intermediate properties. Indeed the measurements of the ^1H free induction decay, and more generally of the different relaxation times in ^1H n.m.r., have proved most useful for investigating microphase-separated block copolymers. For example, in styrene-butadiene block copolymers investigated by Tanaka and Nishi², ^1H free induction decays led to the quantification of hard phase, soft phase and interphasic regions. The interpretation of the spin-lattice relaxation times in the rotating frame, $T_{1\rho}(^1\text{H})$, is based on the spin-diffusion phenomenon, which induces identical relaxation for chemically different species in solid samples provided they are spatially close enough to one another. Non-selective $T_{1\rho}(^1\text{H})$ measurements obtained from wide-line ^1H n.m.r. demonstrated the existence of large interphases in styrene-butadiene block copolymers². More recently, $T_{1\rho}(^1\text{H})$ and free induction decay measurements using both wide-line ^1H n.m.r. and high-resolution solid-state n.m.r. permitted the determination of the extent of interphasic regions as a function of the block molecular weights in a series of styrene-siloxane block copolymers³. In the following sections, we will report results obtained from a combination of n.m.r. techniques on several methylmethacrylate-*n*-butylacrylate diblock and triblock copolymers. We will pay particular attention to the changes that may be observed in the microphase composition of these materials as a function of their thermal history.

EXPERIMENTAL

MATERIALS

The block copolymers were obtained in a two-step process, based on the LPA (ligated anionic polymerization) concept⁴. Methylmethacrylate and *t*-butylacrylate were used together with a monofunctional (diphenylhexyllithium) or difunctional (naphthalene-Li) initiator, ligated by 5-0-molar excess of LiCl⁵. The *r*-butylacrylate units in the obtained copolymers were further transalcoholized using *n*-butyl alcohol in the presence of *paratoluene* sulfonic acid. A more recent study has confirmed the possibility of a direct synthesis from methylmethacrylate and *n*-butylacrylate^{6,7}. The present samples were kindly prepared by the Norsolor Research Center (Verneuil, France). The molecular weights, M_n , of the polymethylmethacrylate (PMMA) and poly(*n*-butylacrylate) (PBuA) homopolymers are 114 600 and 34000, respectively. *Table 1* lists the sample codes, chemical structures, block molecular weights, $M_n(\text{MMA})$ and $M_n(\text{BuA})$, and the percentages of protons contained in each block, $N(\text{MMA})$ and $N(\text{BuA})$ for the copolymers under study. The sample codes refer to the molecular weight of each block in units of 1000. The percentages of *rr*, *mr* and *mm* triads in the MMA blocks and PMMA homopolymer, as determined from ^{13}C n.m.r. in solution, are equal to 72%, 25% and 3%, respectively. The percentages of *rr*, *mr* and *mm* triads in the BuA blocks and PBuA homopolymer are equal to 20%, 52% and 28%, respectively.

The equilibrium morphology of the block copolymers can be qualitatively predicted from the composition of the samples. The M149/B44 sample should exhibit PBuA spheres dispersed in a PMMA matrix. The other block copolymers should exhibit either lamellae or cylinders, the M14/B60 sample being at the border between sphere and cylinder morphologies.

Samples were either powders or films obtained from solvent evaporation of a dioxane solution. They were dried under vacuum at 125°C for 24 h. In the following, these samples are denoted 'as-obtained samples'. Then, the as-obtained samples were annealed at 140°C under vacuum for 72 h to yield the samples denoted 'annealed samples' in the following.

The glass transition temperatures of all the samples were determined by using a DuPont 1090 d.s.c. apparatus, at a 20° min⁻¹ heating rate. Their values are listed in *Table 2*. The glass transition associated with the soft microphase are slightly higher than the PBuA glass transition temperature.

The glass transition temperatures of the hard microphases are equal to or lower than the PMMA glass transition temperature. They somewhat depend on the sample preparation. They increase on annealing. This point will be discussed later.

N.M.R. EXPERIMENTS

¹H relaxation was observed using either wide-line ¹H n.m.r. or high-resolution solid-state ¹³C n.m.r. ¹H free induction decays were obtained at 100 MHz with a Bruker CXP 100 spectrometer using the solid-echo pulse sequence⁸⁻⁹. The 90° pulse length was taken as 2 or 4 μs, depending on the ¹H n.m.r. linewidth. ¹H spin-lattice relaxation times in the rotating frame, $T_{1\rho}(^1\text{H})$, were determined in a 12 Gauss rotating field using the spin-locking pulse sequence. ¹H spin-lattice relaxation times, $T_1(^1\text{H})$, were measured by the inversion-recovery technique 180°, t_{ir} , 90°.

The high-resolution solid-state ¹³C n.m.r. experiments were conducted at 75.47 MHz with a Bruker CXP 300 spectrometer, with quadrature detection and a single r.f. coil which was double tuned for both ¹³C and ¹H. Experiments were carried out using the well-known techniques of proton dipolar decoupling (DD), cross polarization (CP) and magic-angle sample-spinning (MAS). ¹H free induction decays were observed *via* high-resolution solid-state ¹³C n.m.r. using the pulse sequence described in ref. ¹⁰. The pulse sequence used for the $T_{1\rho}(^1\text{H})$ determination was the delayed-contact cross-polarization pulse sequence described in ref. ¹¹. In all these CP-based pulse sequences, the contact duration was 1 ms and the matched spin-lock cross-polarization transfers were carried out with ¹³C and ¹H magnetic field strengths of 63.9 kHz. During the delay time of the delayed-contact cross-polarization pulse sequence, the ¹H magnetic field strength was 63.9 kHz, corresponding to a 15 Gauss rotating field applied to the proton spins. The samples were contained in Al₂O₃ rotors. The spinning speed was around 4000 Hz. Spin-temperature inversion techniques allowed the minimization of baseline noise and roll¹². Flip-back was used to shorten the delay time between two successive pulse sequences¹³.

Table 1 Sample codes, chemical structures, block molecular weights, $M_n(\text{MMA})$ and $M_n(\text{BuA})$, and percentages of protons contained in each block, $N(\text{MMA})$ and $N(\text{BuA})$, for the copolymers under study

Code	Structure	$M_n(\text{MMA})$	$M_n(\text{BuA})$	$N(\text{MMA})$	$N(\text{BuA})$
M14/B60	MMA- <i>b</i> -BuA	14 500	60 000	17	83
M39/B19	MMA- <i>b</i> -BuA	39 400	19 100	64	36
M149/B44	MMA- <i>b</i> -BuA	149 500	44 500	74	26
M22/B62/M22	MMA- <i>b</i> -BuA- <i>b</i> -MMA	2×22500	61 800	38	62

Table 2 Glass transition temperatures (T_g) of the homopolymers and hard and soft microphases of the block copolymers

Sample	Preparation	$T_g(\text{soft})$ (°C)	$T_g(\text{hard})$ (°C)
PMMA			130
PBuA		-45	
M39/B19	As-obtained powder	-42	112
	Annealed powder	-42	124
M14/B60	As-obtained powder	-41	117
	Annealed powder	-39	124
M149/B44	As-obtained powder	-43	124
	Annealed powder	-46	130
	As-obtained film	-47	110
	Annealed film	-42	125
M22/B62/M22	As-obtained powder	-37	124
	Annealed powder	-41	131

RESULTS AND DISCUSSION

POLYMETHYLMETHACRYLATE

The ^1H spin-lattice relaxation of neat PMMA is an exponential function of the time interval, t_{ir} , of the inversion-recovery pulse sequence, 180° , t_{ir} , 90° . It is characterized by a $T_1(\text{H})$ equal to 0.24 s at room temperature, to be compared to the 0.27 s value determined at the same temperature by Parizel *et al.*¹⁴ for a predominantly isotactic PMMA sample with a molecular weight of 62 000, and to the 0.13 s $T_1(\text{H})$ value determined by Naito *et al.*¹⁵.

The PMMA ^1H spin-lattice relaxation in the rotating frame, as determined from wide-line ^1H n.m.r., is an exponential function of time, characterized by a $T_{1\rho}(^1\text{H})$ of 6 ms in the 12 Gauss rotating field. The PMMA $T_{1\rho}(^1\text{H})$ has also been determined by using high-resolution solid-state ^{13}C n.m.r. in a rotating frame of 15 Gauss. It is equal to 9 ms.

It must be noticed that the PMMA $T_{1\rho}(^1\text{H})$ values are highly dependent on both the intensity of the rotating field and the PMMA microstructure. For example, Parizel *et al.*¹⁴ have determined a

15 ms $T_{1\rho}(^1\text{H})$ for a predominantly isotactic PMMA sample in a 15 Gauss rotating field. In a 5.8 Gauss rotating field, Spevacek *et al.*¹⁶ have measured $T_{1\rho}(^1\text{H})$ values of 6.7 and 18 ms for an isotactic and a syndiotactic PMMA, respectively. Naito *et al.*⁵ have determined a 20 ms $T_{1\rho}(^1\text{H})$ value in a 10 Gauss rotating field.

The PMMA 1H free induction decays were determined over the whole temperature range from room temperature to 140°C. Data recorded at 60 and 130°C are shown in *Figure 1* as examples. At temperatures lower than 80°C, they exhibit a rapidly decaying quasi-Gaussian behaviour characteristic of a solid-like behaviour. Above 80°C, the free induction decay has a more complex behaviour, with a quasi-Gaussian behaviour during the first 30 μs and then a slower decay. The $T_2(^1\text{H})$ values, determined from the Gaussian decay are equal to 18 μs at temperatures up to 100°C. Then, they increase rapidly above 107°C, due to the PMMA motions occurring on approaching the glass transition region.

POLY(N-BUTYLACRYLATE)

The spin-lattice relaxations of the PBuA protons in the laboratory and rotating frames are exponential functions of time. At room temperature, they are characterized by a 0.35 s $T_1(^1\text{H})$ and a 2.3 ms $T_{1\rho}(^1\text{H})$, respectively. The 1H free induction decays measured at various temperatures are given in *Figure 2*. Above the glass transition temperature of PBuA, they display a non-exponential time dependence, which was already observed by Folland *et al.*¹⁷ and Cohen-Addad and coworkers¹⁸⁻²¹ on a number of elastomers. In a rubbery compound, such a behaviour is specific to the presence of topological constraints that restrict the amplitude of the molecular motions and induce a residual dipolar interaction. At room temperature, the 1H magnetization decay of PBuA as a function of time, t , can be expressed as:

$$M(t) = M_0 e^{-\left(\frac{t}{T_2}\right)^p} \quad (1)$$

At low temperature, p is equal to 1, and p increases with temperature. It is always lower than 2. The temperature dependence of $T_2(^1\text{H})$, as determined from expression (1), is shown in *Figure 3*.

N.M.R. STUDY OF THE AS-OBTAINED M149/B44 MMA-B-BUA COPOLYMER

In both the film and powder samples, the variation of the $[M(0) - M(t_{\text{ir}})]/2M(0)$ ratio, obtained from wide-line 1H n.m.r., is an exponential function of the time interval, t_{ir} , of the inversion-recovery pulse sequence. It is characterized by a 0.29 s $T_1(\text{H})$ value at room temperature. Therefore, during durations of the order of $T_1(\text{H})$, the spin-diffusion homogenizes the relaxation over the different domains of the samples considered, which indicates that the domain sizes are smaller than 100 Å.

Figure 1 PMMA ^1H free induction decays at 60°C (○) and 130°C (+)

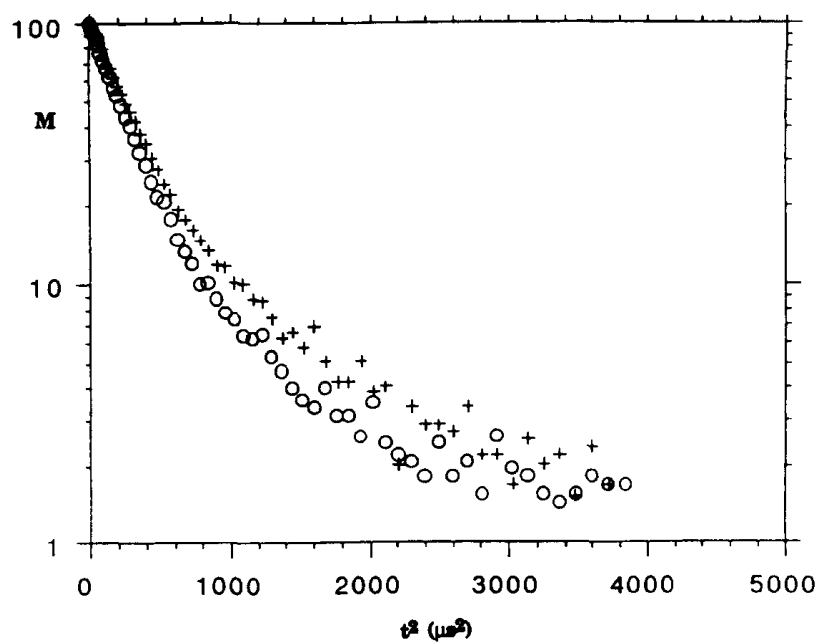


Figure 2 PBuA ^1H free induction decays at different temperatures

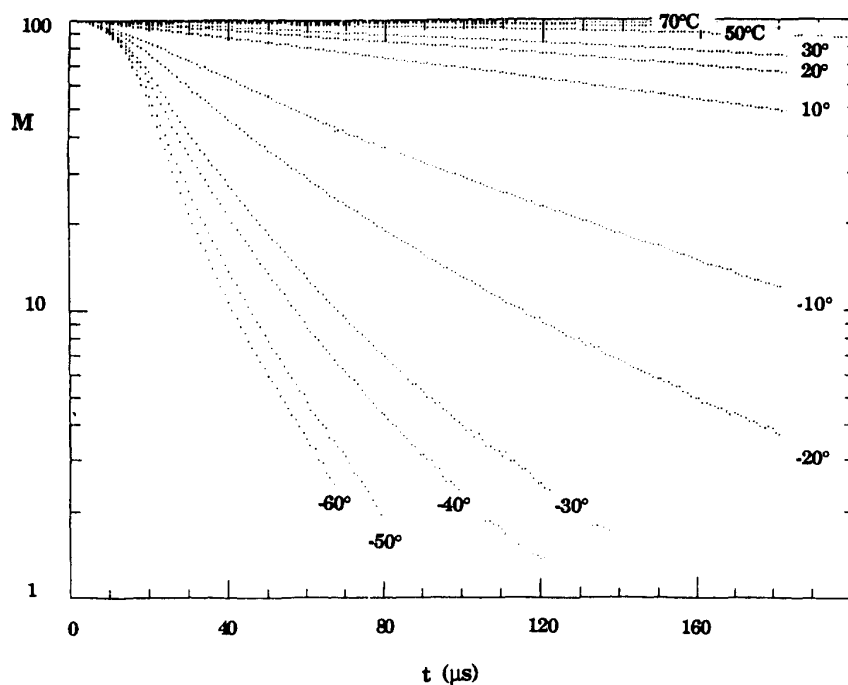
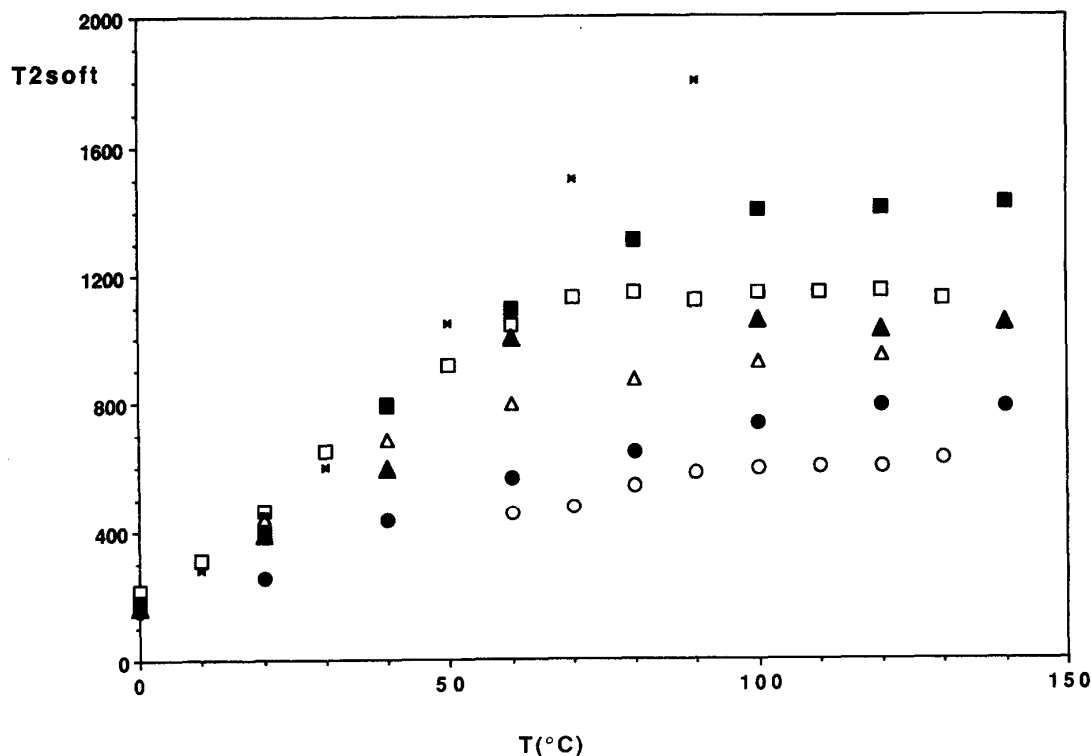


Figure 3 Temperature dependences, as determined from expression (1), of $T_2(^1\text{H})$ in PBuA (\times), and $T_{2\text{soft}}$ in M14/B60 (\square, \blacksquare), M39/B49 (\circ, \bullet) and M22/B62/M22 ($\triangle, \blacktriangle$) copolymers. Open symbols, as-obtained samples; filled symbols, annealed samples



The magnetization decays in a spin-lock experiment, obtained from wide-line ^1H n.m.r. in a 12 Gauss rotating field at room temperature, do not exhibit a simple exponential behaviour. As a first approximation, they can be considered as the sum of two exponential functions with $T_{1\rho}(^1\text{H})$ s of the order of 2.2 and 6.5 ms. These values are very close to the $T_{1\rho}(^1\text{H})$ s of the homopolymers and, thus, can be associated to the soft and hard microphases, respectively. Therefore, in this copolymer, the sizes of the two microphases are too large for the spin diffusion mechanism to homogenize the spin-lattice relaxation in the rotating frame over the whole sample. By comparing the $T_1(^1\text{H})$ and $T_{1\rho}(^1\text{H})$ behaviours, one is led to the conclusion that the sizes of the domains are in the range from 10 to 100 Å, in agreement with the values of the radii of gyration that are calculated from the lengths of each block. It must be noticed that no interphase is detected in these $T_1(^1\text{H})$ and $T_{1\rho}(^1\text{H})$ experiments, which indicates that the interphase dimensions are less than 10 Å.

Determinations of the ^1H spin-lattice relaxation times in the rotating frames at room temperature were also performed by using high-resolution solid-state ^{13}C n.m.r. in a 15 Gauss rotating field. Since these measurements were based on cross-polarization, they mainly probe the hard microphase. Results reported in *Figure 4* for the MMA units indicate that, in the rigid block, $T_{1\rho}(^1\text{H})$ is equal to 8.5 ms, i.e. slightly smaller than in the neat PMMA homopolymer, which is the first indication that the rigid microphase contains some BuA units. Moreover, as shown in *Figure 4*, the $T_{1\rho}(^1\text{H})$ decay somewhat departs from its monoexponential character at short

times, implying that there are some heterogeneities in the hard microphase composition of the as-obtained samples.

Figure 4 $T_{1\rho}(^1\text{H})$ decays as obtained from high-resolution solid-state ^{13}C n.m.r. and averaged over the different MMA ^{13}C n.m.r. peaks, on the as-obtained (\circ) and annealed (\bullet) M149/B44 samples. Lines are guides for the eye

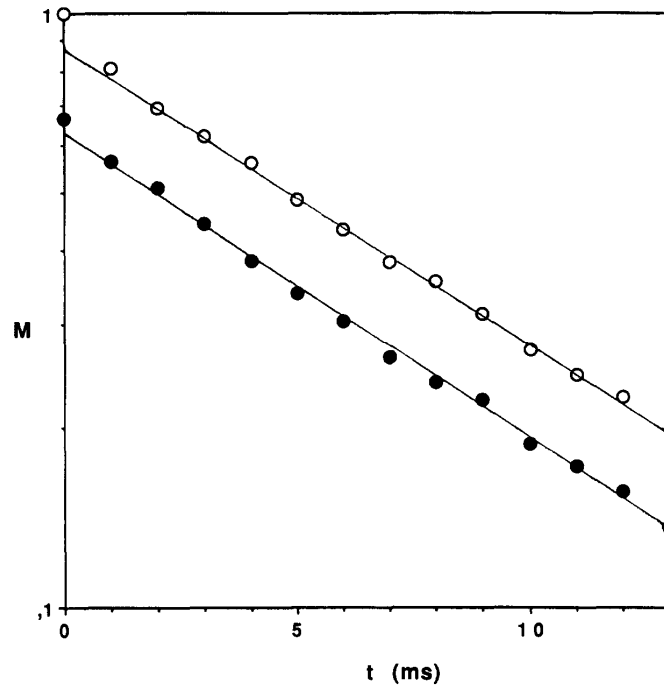
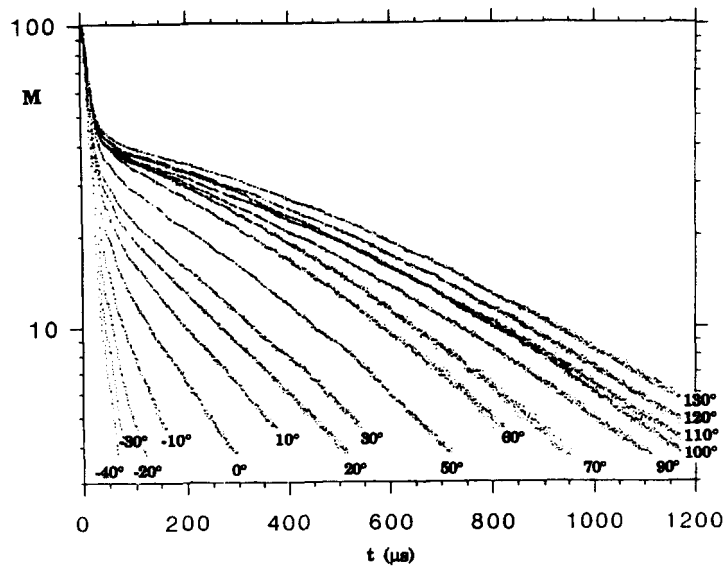


Figure 5 ^1H free induction decays determined at different temperatures for the as-obtained M149/B44 powder



The ^1H free induction decays obtained at different temperatures for the as-obtained powder are displayed in *Figure 5*. At very low temperatures, they exhibit a quasi-Gaussian behaviour, in agreement with the solid character of both blocks. At temperatures above 0°C , in both powder and film samples, the free induction decays exhibit a fast and a slow relaxing component, which correspond to rigid and mobile protons, respectively. The slow relaxing component can be assigned to the protons of the soft BuA microphases above their glass transition temperature. As observed in the PBuA homopolymer and shown by the example of the as-obtained M149/B44 MMA-*b*-BuA copolymer at 30°C given in *Figure 6a*, the time dependence of the ^1H free induction decay of the slow relaxing component is well-described by expression equation (1).

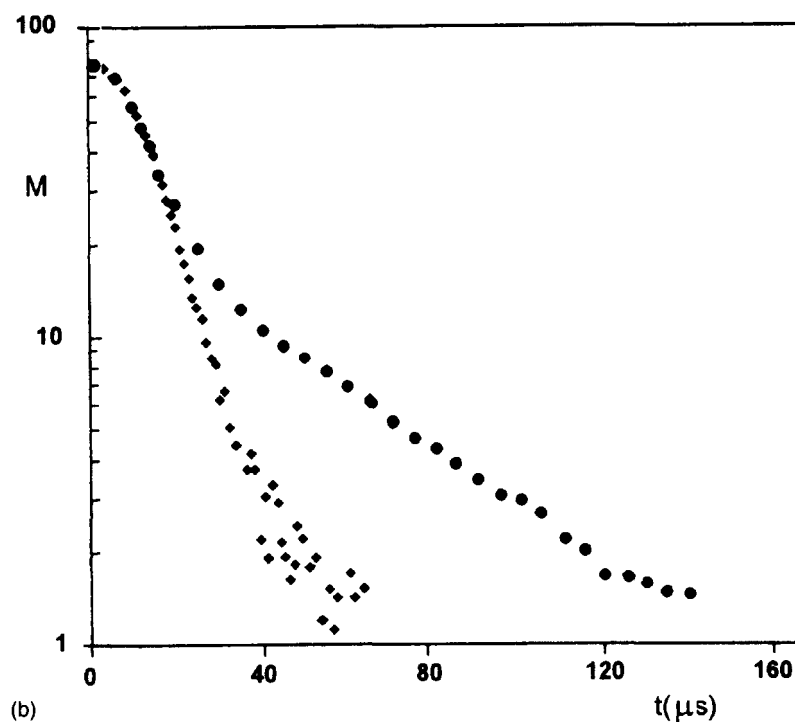
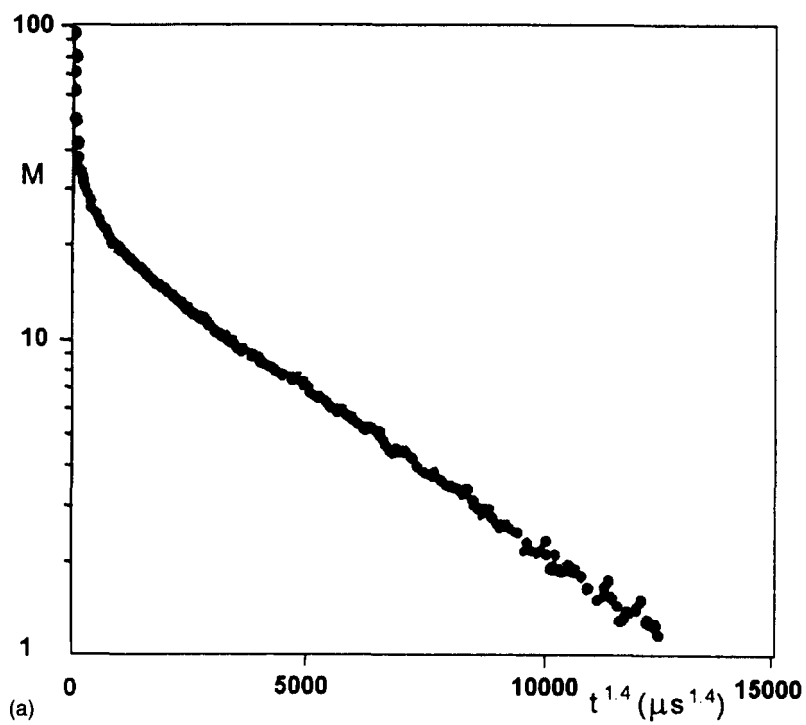
The relative amount of mobile protons is determined by extrapolating the slow relaxing component to zero time. Comparison of the PMMA ^1H free induction decay with the copolymer fast relaxing component, obtained after subtracting the slow relaxing component from the ^1H free induction decay, is shown in *Figure 6b*. At short times, the homopolymer and copolymer exhibit a very similar Gaussian decay which thus can be assigned to the protons in the hard MMA microphase. At longer times, the difference between the two signals can be attributed to protons belonging to a phase of intermediate mobility, i.e. a mixed phase or an interphase. As shown in *Figure 6b*, these protons are characterized by an exponential free induction decay, within experimental accuracy.

Therefore, as a first approximation, the ^1H free induction decay of the M149/B44 MMA-*b*-BuA copolymer can be considered as the sum of three components. In the temperature range from 0°C to 130°C where the spin-spin relaxation times of the three components of the free induction decay are very different, the free induction decay is well represented by the sum of the following three components:

$$M_x(t) = N_{\text{hard}} e^{-\left(\frac{t}{T_{2\text{hard}}}\right)^2} + N_{\text{inter}} e^{-\left(\frac{t}{T_{2\text{inter}}}\right)} + N_{\text{soft}} e^{-\left(\frac{t}{T_{2\text{soft}}}\right)^p} \quad (2)$$

where $T_{2\text{hard}}$, $T_{2\text{inter}}$ and $T_{2\text{soft}}$ are the spin-spin relaxation times of the three components, and N_{hard} , N_{inter} and N_{soft} are the percentages of protons in the different microphases. The existence of a phase with intermediate mobility is also supported by determinations of the ^1H free induction decays at room temperature obtained by using high-resolution solid-state ^{13}C n.m.r. and shown in *Figure 7* for the MMA and BuA nuclei, respectively. The MMA nuclei exhibit a quasi-Gaussian behaviour during the first $30 \mu\text{s}$, with a $T_2(^1\text{H})$ close to the PMMA $T_2(^1\text{H})$. Then, the MMA nuclei have a slower decay, which can be assigned to more mobile MMA units. This signal is quite weak. However, it must be noticed that the MMA units in the hard microphase are predominant and that the cross-polarization experiment accentuates the contribution of the most rigid species. The magnetization decay of the BuA units is much slower.

Figure 6 (a) ^1H free induction decay determined at 30°C for the as-obtained M149/B44 powder, (b) Comparison of the PMMA ^1H free induction decay (\blacklozenge) with the copolymer fast relaxing component (\bullet), obtained after subtracting the slow relaxing component from the ^1H free induction decay



It can be approximated by a sum of two components. In agreement with results derived from the analysis of directly measured ^1H free induction decays, the slower decay observed at long times can be assigned to mobile BuA units located in the soft microphase, whereas more rigid BuA

units situated in a mixed phase are responsible for the faster decay of the BuA units observed at short times.

Values of the $T_{2\text{hard}}$, $T_{2\text{inter}}$ and $T_{2\text{soft}}$ spin-spin relaxation times and amounts of protons in the different microphases, N_{hard} , N_{inter} and N_{soft} , derived from the analysis of the H free induction decays in terms of expression (2), are plotted in *Figures 8 and 9*, respectively, as a function of temperature for the as-obtained powder and film. The spin-spin relaxation times associated with the hard microphase do not depend on temperature, in the temperature range considered. They are strictly identical to the glassy PMMA $T_2(^1\text{H})$ relaxation time. At temperatures higher than 50°C, the spin-spin relaxation times associated with the soft microphase are somewhat lower than those determined for the neat PBuA homopolymer under similar temperature conditions (*Figure 3*).

Figure 7 ^1H free induction decays at room temperature obtained by using high-resolution solid-state ^{13}C n.m.r. for the MMA (●, $\text{C}\beta$ carbon; ▲, CH_3 carbon; X, OCH_3 , carbon) and BuA nuclei (O, $\text{C}\beta$ carbon; □, CH_3 carbon) respectively, of the as-obtained M149/B44 copolymer

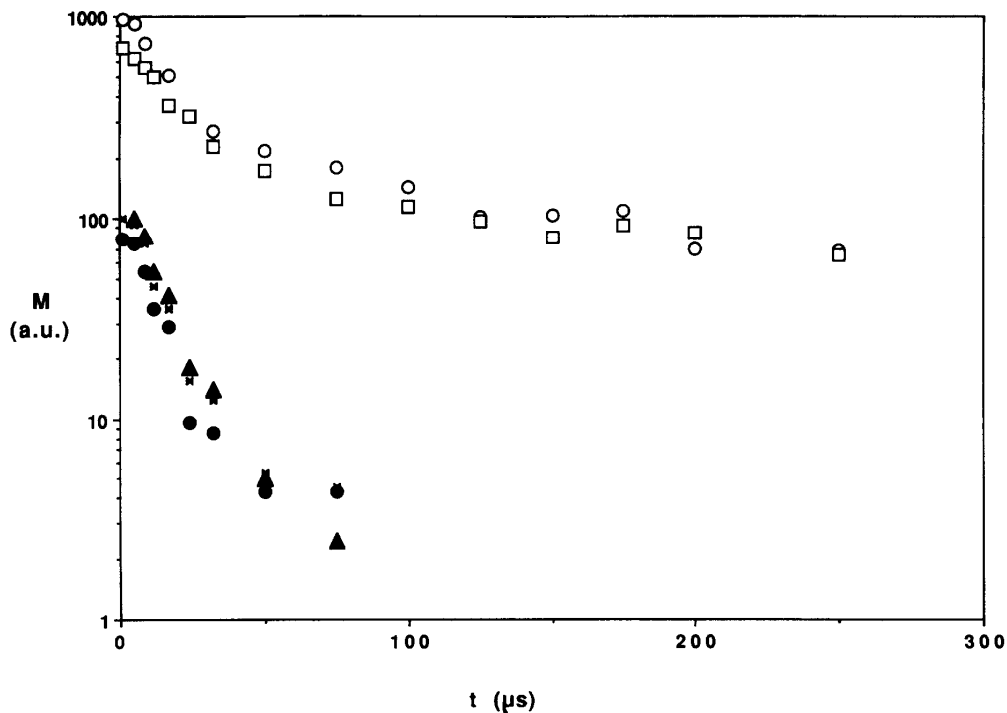


Figure 8 Values of $T_{2\text{hard}}$ (□,■), $T_{2\text{inter}}$ (Δ,▲) and $T_{2\text{soft}}$ (●,○) spin-spin relaxation times in the as-obtained M149/B44 samples. Open symbols, film; filled symbols, powder

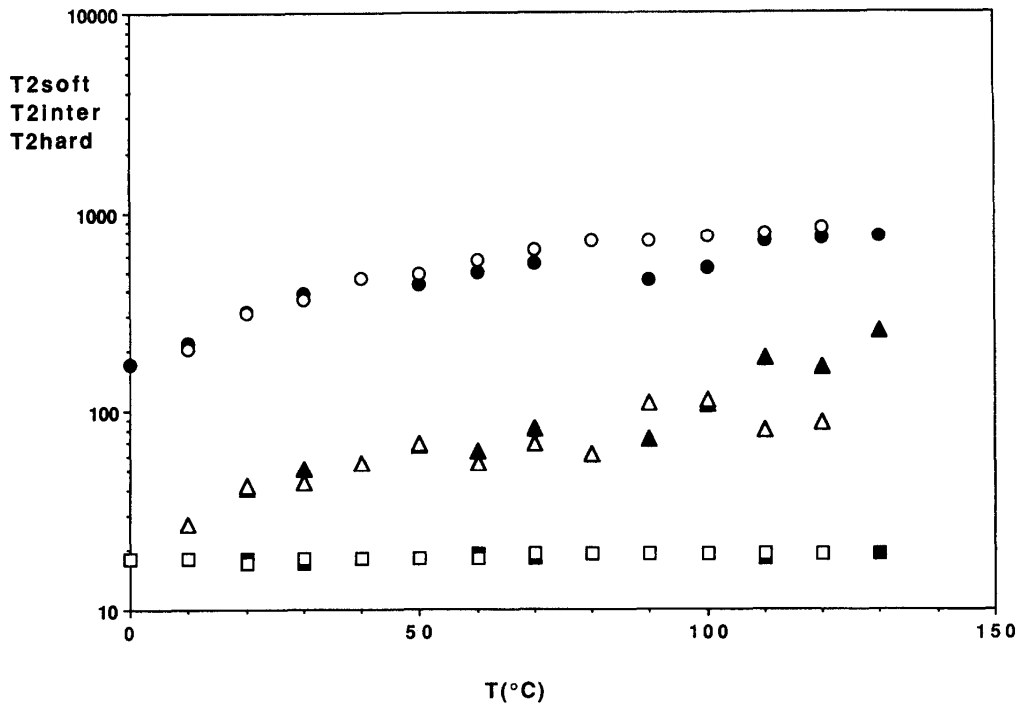
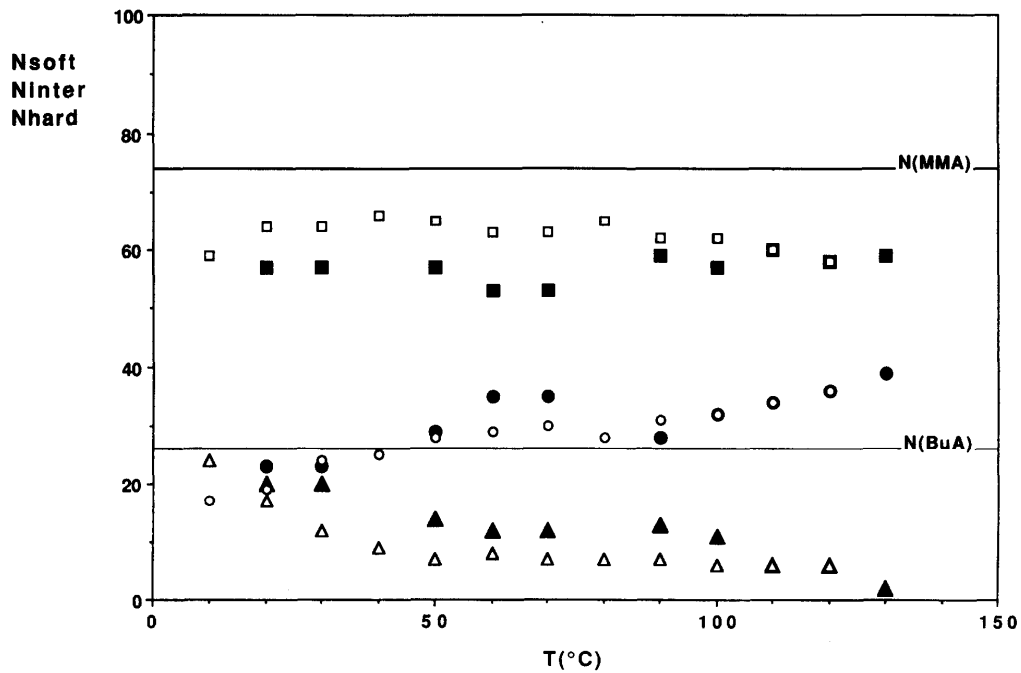


Figure 9 Amounts of protons in the different microphases of the as-obtained MI 49/B44 samples, N_{hard} (\square, \blacksquare), N_{inter} (Δ, \blacktriangle) and N_{soft} (\circ, \bullet), derived from the analysis of the ^1H free induction decays in terms of expression (2). Open symbols, film; filled symbols, powder

In both the powder and film samples, the spin-spin relaxation times of the three components are



very different at temperatures above 50°C , which implies that the amount of protons contained in each of the three phases can be determined quite accurately. Between 50 and 100°C , the $T_{2\text{inter}}$ relaxation time has nearly no dependence on temperature. Besides, in this temperature range,

the compositions of the soft and hard microphases and interphase are constant. The number of protons contained in the hard phase in both samples is significantly lower than the amount of MMA protons in the MMA block, $N(\text{MMA})$. The amount of soft phase is somewhat higher than the amount of BuA protons, $N(\text{BuA})$. Therefore, at these temperatures, there must exist MMA units in the three phases of the copolymer. This analysis is consistent with the rather low observed $T_{2\text{soft}}$ values that indicate that the motions of the BuA units are slowed down by the presence of MMA units in the soft phase.

Above 100°C, $T_{2\text{inter}}$ increases, N_{inter} decreases and N_{soft} increases. Variations in the microphase compositions are also observed at temperatures below 50°C. Such behaviours can be related to the heterogeneous character of the interphasic regions: on increasing temperature, the soft units and the more mobile units in the interphasic regions of the powder tend to have a similar behaviour, so that the separation between these two types of units is no longer clean-cut. Similarly, at lower temperatures, the differences in the behaviours of the hard microphase and more rigid units of the interphase tend to disappear.

A more detailed investigation of *Figures 8 and 9* shows that, at temperatures below 110°C, the spin-spin relaxation times associated with the interphase and soft microphase slightly depend on the sample, powder or film, under study. Besides, the microphase compositions of the film and powder (*Figure 9*) are not strictly identical. The amounts of soft and intermediate phases are higher and the rigid microphase is less extended in the powder than in the film. When considering the composition variations above 100°C, the interphasic regions seem to be more heterogeneous in the powder than in the film. All these observations must also be related to the dependence of the glass transition temperature, as observed from d.s.c, on the sample preparation.

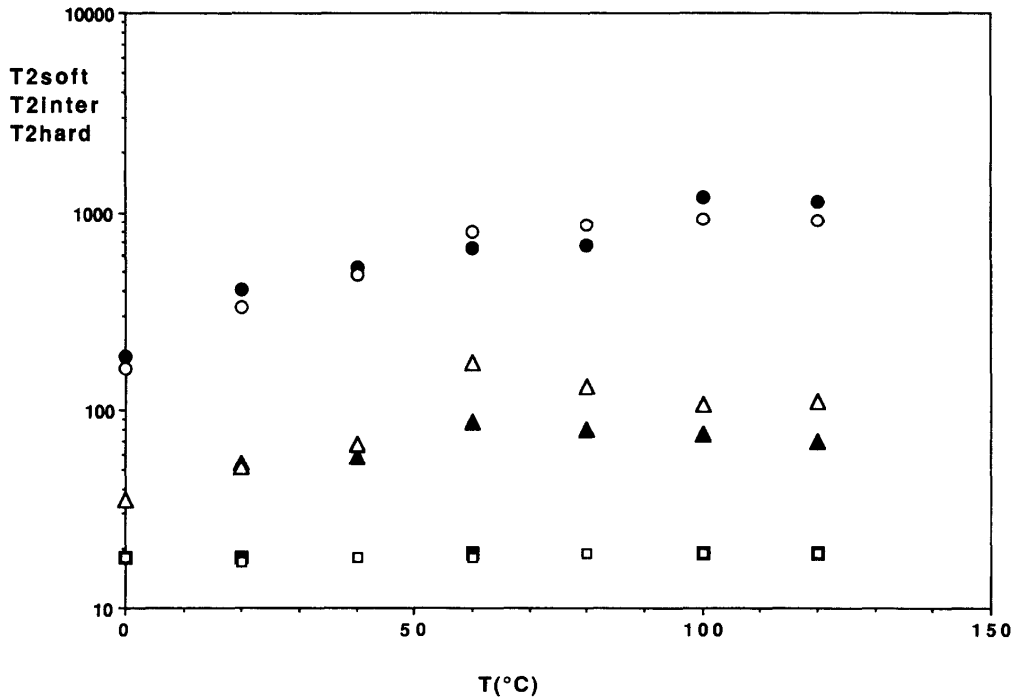
N.M.R. STUDY OF THE ANNEALED M149/B44 MMA-B-BUA COPOLYMER SAMPLES

The values of the spin-spin relaxation times and percentages of protons in the different microphases, as determined from the analysis of the free induction decay using expression (2), are plotted in *Figures 10 and 11*, respectively for the annealed M149/B44 samples as a function of temperature.

As shown in these figures, on annealing, the extent of the soft microphase is significantly increased to the detriment of the hard phase. Besides, the annealing of the sample induces a small increase in the mobility of the soft microphase. These results show that the soft microphases contain a larger amount of BuA units in the annealed samples than in the as-obtained samples. In the case of the M149/B44 copolymer, this BuA enrichment of the soft microphase must originate from diffusion of BuA units from the hard microphase to the soft domains since the characteristics of the intermediate phase are not markedly modified. Only, the temperature dependence of the extent of interphasic region is considerably reduced as compared to the behaviour of the as-obtained samples, which tends to indicate a less heterogeneous character of that region.

The effect of annealing on the microphase homogeneity is also demonstrated in *Figure 4* by the monoexponential character of the $T_{1\rho}(^1\text{H})$ decay of the MMA units in the hard microphase determined by using high-resolution solid-state ^{13}C n.m.r.

Figure 10 Values of $T_{2\text{hard}}$ (\square, \blacksquare), $T_{2\text{inter}}$ (Δ, \blacktriangle) and $T_{2\text{soft}}$ (\circ, \bullet) spin-spin relaxation times in the annealed M149/B44 samples. Open symbols, film; filled symbols, powder



After annealing, the differences between the film and powder tend to disappear. It must be noticed that the differences observed for the as-obtained samples cannot be explained on the basis of their chemical structure. A likely interpretation is that, before annealing, the samples are not at thermodynamic equilibrium. The organization of the chains may have been partially frozen during the sample preparation. Then, on annealing the sample at high temperature, the chains recover an increased mobility. They can diffuse, reorganize themselves and approach their thermodynamical equilibrium which is identical for the powder and film. As previously observed from data plotted in *Figures 10 and 11*, it is of interest to note that the annealing is particularly efficient for the mobile BuA blocks which can leave the hard microphase in which they had been trapped during the sample preparation. In contrast, the MMA blocks, which are very long in the M149/B44 copolymer, are much less mobile and, therefore, diffuse much more slowly. As a consequence, they should be less affected by annealing. As indicated in *Figure 11* by the comparison of N_{hard} and N_{soft} with $N(\text{MMA})$ and $N(\text{BuA})$, respectively, the soft microphase still contains a significant number of MMA units after annealing. This conclusion is also supported by the $T_{2\text{soft}}$ values that are shorter than the PBuA T_2 (^1H)s under similar temperature conditions (*Figure 3*).

N.M.R. STUDY OF THE M14/B60 AND M39/B19 MMA-B-BUA COPOLYMERS AND M22/B62/M22 MMA-B-BUA-B-MMA TERPOLYMER

The ^1H free induction decays of the as-obtained and annealed M14/B60 and M39/B19 diblock copolymers and M22/B62/M22 triblock copolymer strongly differ from the sum of the contributions of their neat components. They exhibit a three-component behaviour on a large temperature range. The values of the $T_{2\text{soft}}$ and $T_{2\text{inter}}$ spin-spin relaxation times and the percentage of protons in the different microphases, determined from the free induction decay analysis in terms of expression (2) are displayed in *Figures 3, 12-15* as a function of temperature for the different samples. The $T_{2\text{hard}}$ spin-spin relaxation time is identical to the glassy PMMA $T_2(^1\text{H})$ over the temperature range investigated.

As shown by the weak temperature dependence of the phase compositions in the annealed sample and the monoexponential character of the $T_{1\rho}(^1\text{H})$ decay of the MMA units in the hard microphase, as determined by using high-resolution solid-state ^{13}C n.m.r., annealing improves the microphase homogeneity.

As previously observed for the M149/B44 block copolymer, annealing also slightly increases the mobility of the soft microphase in all the samples considered. Simultaneously, it induces an increase of the extent of the soft microphase to the detriment of the intermediate and hard phases. These changes in the bulk organization of the block copolymers on annealing indicate that the as-obtained samples are far from thermodynamic equilibrium. On annealing at high temperature, the mobile BuA units have a high mobility. They can leave the hard and intermediate microphases where they had been trapped during the sample preparation, and diffuse into the soft regions.

As shown in *Figures 13-15*, in all the annealed samples investigated, the amount of rigid microphase is always smaller than the amount of MMA protons, $N(\text{MMA})$, contained in the sample. The amount of mixed phase, N_{inter} , is quite similar in all the samples considered. The $T_{2\text{inter}}$ values depend on the block copolymer composition. Their order of magnitude indicates that the mixed phase has a much lower mobility than the soft microphase and, therefore, the interphase must be relatively enriched in MMA units.

Figure 11 Amounts of protons in the different microphases of the annealed M149/B44 samples, N_{hard} (\square, \blacksquare), N_{inter} (Δ, \blacktriangle) and N_{soft} (\circ, \bullet), derived from the analysis of the ^1H free induction decays in terms of expression (2); Open symbols, film; filled symbols, powder

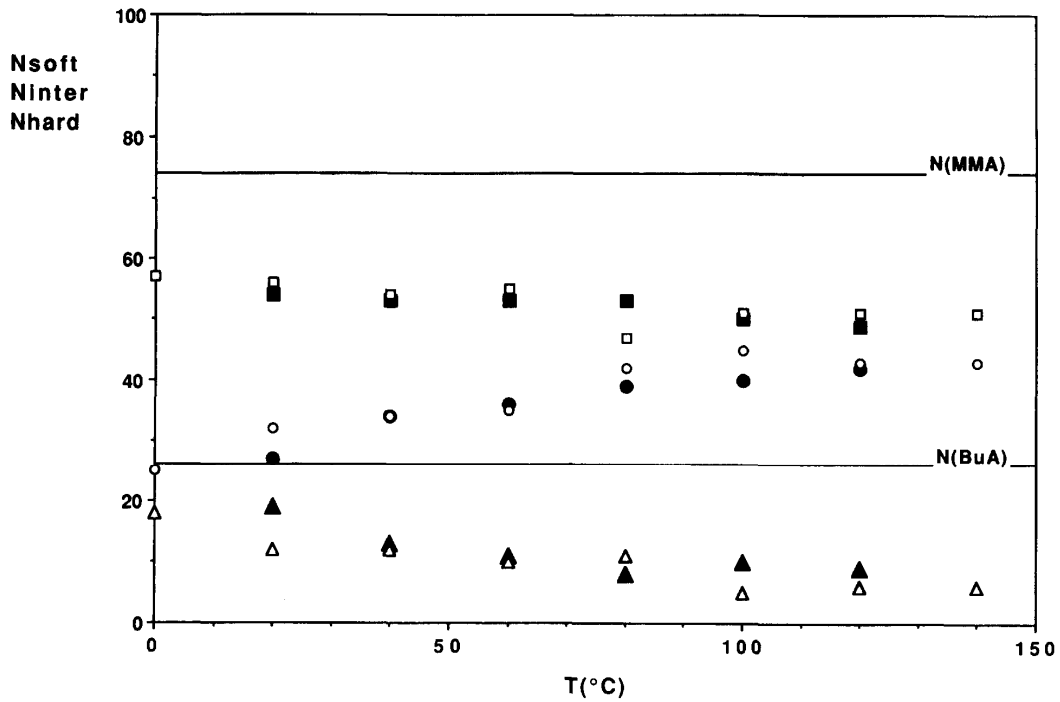


Figure 12 Values of $T_{2\text{inter}}$ in M14/B60 (\square, \blacksquare), M39/B60 (\circ, \bullet) and M22/B62/M22 (Δ, \blacktriangle) copolymers. Open symbols, as-obtained samples; filled symbols, annealed samples

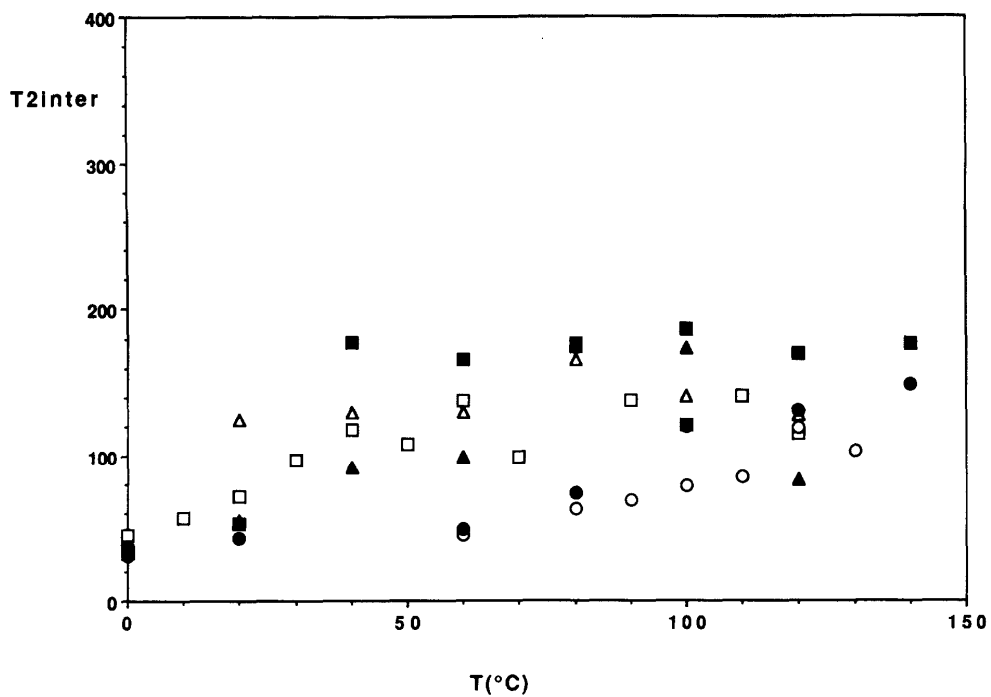
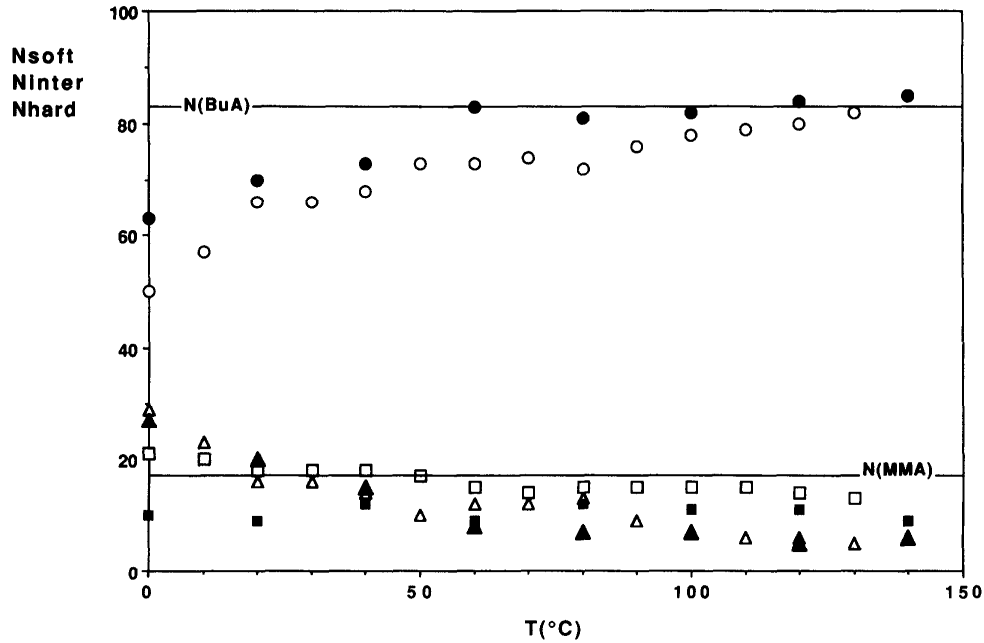
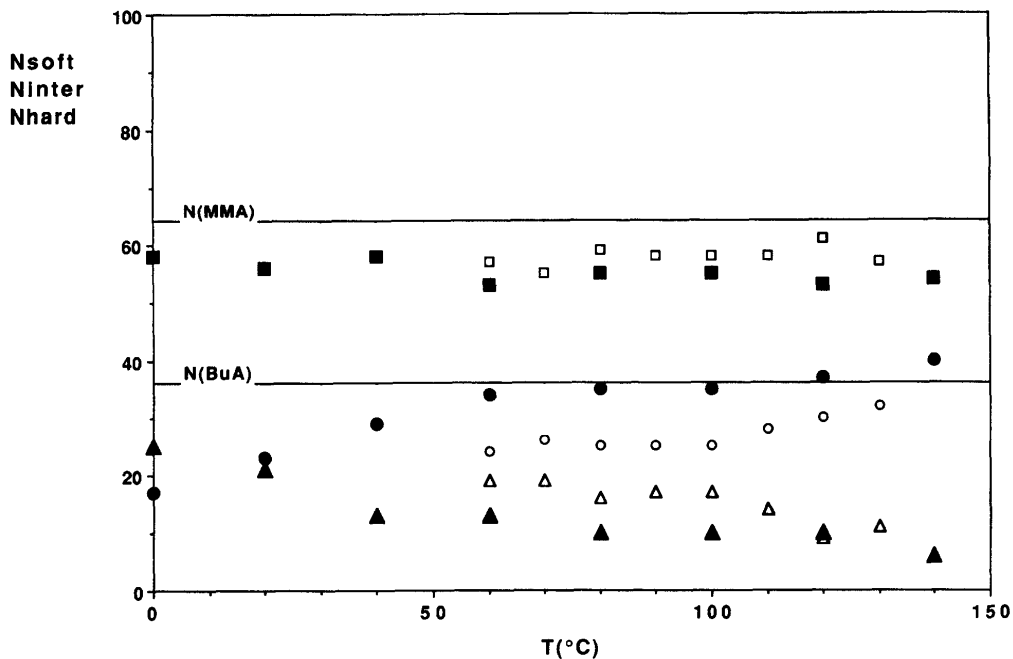


Figure 13 Amounts of protons in the different microphases of the M14/B60 MMA-*b*-BuA samples, N_{hard} (\square, \blacksquare), N_{inter} (Δ, \blacktriangle) and N_{soft} (\circ, \bullet), derived from the analysis of the ^1H free induction decays in terms of expression (2). Open symbols, as-obtained sample; filled symbols, annealed sample



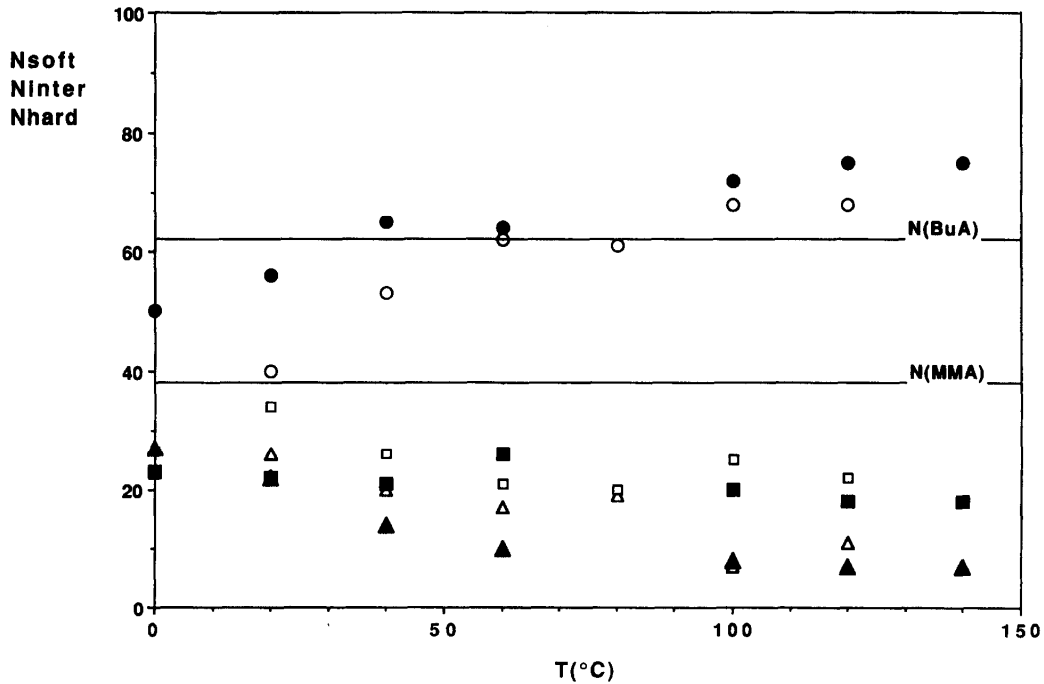
annealed sample

Figure 14 Amounts of protons in the different microphases of the M39/B19 MMA-*b*-BuA samples, N_{hard} (\square, \blacksquare), N_{inter} (Δ, \blacktriangle) and N_{soft} (\circ, \bullet), derived from the analysis of the ^1H free induction decays in terms of expression (2). Open symbols, as-obtained sample; filled symbols, annealed sample



annealed sample

Figure 15 Amounts of protons in the different microphases of the M22/B62/M22 samples, N_{hard} (\square, \blacksquare), N_{inter} (Δ, \blacktriangle) and N_{soft} (\circ, \bullet), derived from the analysis of the ^1H free induction decays in terms of expression (2). Open symbols, as-obtained sample; filled symbols, annealed sample



The relative extent of the soft microphase and $T_{2\text{soft}}$ values are quite different in the various annealed block copolymers under study. Whereas, in the plateau region, the amounts of soft microphase in the M149/B44 copolymer and in the triblock copolymer are clearly higher than the amount of BuA protons contained in the sample, $N(\text{BuA})$, the amount of soft microphase is identical to the amount of BuA protons contained in the sample in the M14/B60 and M39/B19 samples. Therefore, the relative amount of MMA units located in the soft microphase is much lower in the M14/B60 and M39/B19 samples than in the M149/B44 block copolymer. This result must be related to the fact that, as compared to the M14/B60 and M39/B19 samples, the MMA blocks in the M149/B44 copolymer are very long and require a much longer time to diffuse over a given distance and leave the mixed or soft microphase. Diffusion of the MMA blocks of the triblock copolymer is also comparatively slow.

These conclusions are supported by the $T_{2\text{soft}}$ values plotted in *Figure 3*: in the M14/B60 copolymer, whose soft microphase contains only a very small number of MMA units, the mobility of the soft microphase, as indicated by its $T_{2\text{soft}}$ value, is indeed very close to the PBuA mobility. When the amount of MMA units in the soft microphase increases, as previously observed for the M149/B44 copolymer and for the terpolymer, a decrease in the $T_{2\text{soft}}$ values, and, therefore, in the soft microphase mobility, is observed. In the M39/B19 copolymer, the amounts of protons in the rigid and mixed phase tend to indicate that the soft microphase contains only a very few MMA units.

In contrast, the mobility of the soft microphase is significantly lower than the mobility of the PBuA homopolymer. This result may be due to the fact that the BuA blocks in the M39/ B19 sample are very short and, therefore, they are more sensitive to the MMA neighbourhood.

These differences in microphase compositions between the as-obtained and annealed samples may be considered as responsible for most of the variations of the glass transition temperatures observed in *Table 2* for the hard microphase. On annealing, the glass transition temperature of the hard microphases systematically increases, in agreement with the departure of some of the BuA units contained in this phase. With respect to the soft microphase, the glass transition temperatures of the as-obtained and annealed samples are very close to each other. They can be considered as equal within experimental accuracy, and therefore, as compared to d.s.c, the n.m.r. technique appears to be a much more accurate tool for investigating the soft microphase composition.

ACKNOWLEDGEMENTS

Financial support by BRITE (RI 1B-0227) program is gratefully acknowledged. The authors thank Drs P. Heim and P. Gaillard (Elf Atochem company) for the synthesis of the block copolymers.

REFERENCES

1. Soltani, R., Ph.D. thesis, Université Pierre et Marie Curie, 1992.
2. Tanaka, H. and Nishi, T., *Phys. Rev. B*, 1986, 33, 32.
3. Soltani, R., Laupretre, F., Monnerie, L. and Krause, S., *Polymer*, 1995, 36, 275.
4. Wang, J. S., Jérôme, R. and Teyssié, P., *J. Phys. Org. Chem.*, 1995, 8, 208.
5. Varshney, S. K., Jacobs, C, Hautekeer, J. P., Bayard, P., Jérôme, R., Fayt, R. and Teyssié, P., *Macromolecules*, 1991, 24, 4997.
6. Nugay, N., Nugay, T., Jérôme, R. and Teyssié, P., *J. Polym. Sci., Polym. Chem. Ed.*, 1997, **35**, 361.
7. Nugay, N., Nugay, T., Jérôme, R. and Teyssié, P., *J. Polym. Sci., Polym. Chem. Ed.* in press,.
8. Mansfield, P., *Phys. Rev.*, 1963, **137**, 961.
9. Jeener, J. and Broekaert, P., *Phys. Rev.*, 1967, **157**, 232.
10. Tékély, P., Canet, D. and Delpuech, J., *Mol. Phys.*, 1989, 67, 81.
11. Stejskal, E. O., Schaefer, J., Sefcik, M. D. and McKay, R. A., *Macromolecules*, 1981, 14, 275.
12. Stejskal, E. O. and Schaefer, J., *J. Magn. Reson.*, 1975, 18, 560.
13. Tegenfeldt, J., Haeberlen, U. and Waugh, J. S., *J. Magn. Reson.*, 1979, 36, 453.
14. Parizel, N., Lauprêtre, F. and Monnerie, L., *Polymer*, 1997, 38, 3719.
15. Naito, K., Johnson, G. E., Allara, D. L. and Kwei, T. K., *Macromolecules*, 1978, 11, 1261.
16. Spevacek, J., Schneider, B. and Straka, J., *Macromolecules*, 1990, 23, 3042.

17. Folland, R., Steven, J. H. and Charlesby, A., *J. Polym. Sci., Polym. Phys. Ed.*, 1978, 16, 1041.
18. Martin-Borret, Y. and Cohen-Addad, J. P.. *J. Chem. Phys.*, 1973, 58, 1700.
19. Cohen-Addad, J. P., Domard, M. and Boileau, S.. *J. Chem. Phys.*, 1981, 75, 4107.
20. Cohen-Addad, J. P., *Polymer*, 1983, 24, 1128.
21. Cohen-Addad, J. P. and Dupeyre, R., *Polymer*, 1983, 24, 400.