Macromolecules **2005,** *38,* 4377−4383

Molecular Orientation and Relaxation in Uniaxially Stretched Segmented PTMO Zwitterionomers by Polarization Modulation Infrared Linear Dichroism

Yanxiang Wang,[†] Christian Pellerin,[‡] C. Geraldine Bazuin,[*,‡] and Michel Pézolet[*]

Centre de recherche en sciences et ingénierie des macromolécules (CERSIM), Département de chimie, Université Laval, Cité universitaire, Québec, Canada G1K 7P4

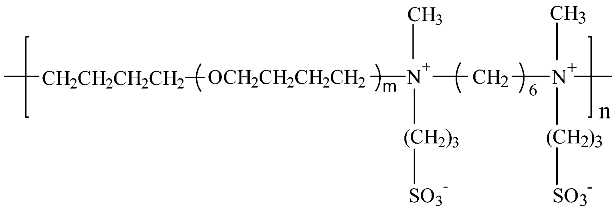
Received December 23, 2004; Revised Manuscript Received March 17, 2005

ABSTRACT: The orientation and relaxation behavior of segmented poly(tetramethylene oxide) (PTMO) zwitterionomers was studied under conditions where no strain-induced crystallization occurs, using polarization modulation infrared linear dichroism. Samples of three different PTMO segment lengths, designated Z67, Z52, and Z20 for PTMO blocks with molar masses of 6700, 5200, and 2000 g/mol, respectively, were used. During deformation to a draw ratio of 3.2, the PTMO chains progressively orient along the stretch direction, the maximum induced orientation decreasing with increase in temperature. In contrast, the orientation function of the sulfonate units increases only at the beginning of the deformation process, reaching a maximum of about 0.015 at a draw ratio of about 1.5, and then decreases to become negative before the end of the stretch period. During the subsequent relaxation period, the PTMO orientation decreases as a function of time and the negative orientation function of the ionic groups further decreases slightly with time. By analogy with segmented copolymers characterized by a crystalline hard phase and an elastomeric soft phase, the following model is proposed. Before deformation, the ionic aggregates, which have previously been shown to have lamellar (Z20) or hexagonal (Z52, Z67) morphology, are like rigid anisotropic entities randomly oriented throughout the sample. Upon deformation to low draw ratios, the flexible PTMO chains orient along the stretch direction and the ionic rigid entities orient perpendicular to the stretch direction, the latter entailing orientation of the ionic side chains parallel to the stretch direction. At higher draw ratios, the applied stress causes progressive disruption of the ionic aggregates, resulting in a reorientation of the "freed" ionic side chains perpendicular to the deformation direction.

Introduction

A series of homologous segmented poly(tetramethylene oxide) (PTMO) zwitterionomers with the chemical structure shown in Scheme 1 were previously synthesized and characterized by Galin and co-workers.[1−3] It was shown that strong ionic interactions lead to the formation of a biphasic morphology (two glass transitions) characterized by the dispersion of hard microdomains composed of virtually all of the polar zwitterionic units and about 10−30% of the weakly polar PTMO segments (high-T_g phase) within a soft matrix composed of pure PTMO (low-T_g phase). This two-phase structure is concordant with the well-known ionomer morphology, which has been discussed extensively in the literature.[4−6] Compared to statistical zwitterionomers,[7] the regular distribution of the ionic units of the segmented zwitterionomers results in some new properties, such as a much better segregation of the hard and soft phases [detected by differential scanning calorimetry (DSC) and solid-state nuclear magnetic resonance (NMR)[2]] and long-range order of the ionic aggregates [detected by small-angle X-ray (SAXS) and neutron (SANS) scattering[3]]. The PTMO zwitterionomers have a lamellar morphology for shorter PTMO blocks and a hexagonal morphology for longer PTMO blocks.[3]

Scheme 1



$$\left[CH_2CH_2CH_2CH_2 \left(OCH_2CH_2CH_2CH_2 \right)_m \underset{\underset{SO_3^-}{(CH_2)_3}}{\overset{CH_3}{N^+}} \left(CH_2 \right)_6 \underset{\underset{SO_3^-}{(CH_2)_3}}{\overset{CH_3}{N^+}} \right]_n$$

We have recently investigated the phenomenon of strain-induced crystallization in one of these segmented zwitterionomers by infrared linear dichroism.[8] Molecular orientation and relaxation, in general, have been studied in single-phase polymers,[9−13] in ionomers,[14−20] and in other multiphase polymer systems.[21−27] In this paper, we have investigated the orientation and relaxation behavior of three zwitterionomers of different PTMO segment lengths (designated Z20, Z52, and Z67 for segmental PTMO molar masses of 2000, 5200, and 6700 g/mol, respectively), mainly under conditions where no strain-induced crystallization occurs. This has allowed us to focus on correlations between the noncrystalline morphology and the orientation−relaxation behavior. Polarization modulation (PM) has recently been used for in situ measurements of infrared linear dichroism (IRLD).[28−33] It has been shown that PM-IRLD is highly effective for determining quantitatively the segmental orientation in polymers, especially for samples showing a low level of orientation.[12,34] In addition, PM-IRLD offers good time resolution, which is especially important for following the relaxation behavior at the beginning of the decay. The orientation of the ionic

---

[†] Current address: Biology Department, McMaster University, Hamilton (ON), Canada L8S 4K1.

[‡] Current address: Département de chimie, Université de Montréal, C. P. 6128, Succ. Centre-Ville, Montréal (QC), Canada H3C 3J7.

[*] Corresponding authors. E-mail: michel.pezolet@chm.ulaval.ca; geraldine.bazuin@umontreal.ca.

10.1021/ma047330e CCC: $30.25

Table 1. Basic Characteristics of Z67, Z52, and Z20, As Obtained from Refs 1 and 2[a]

sample	$M_n^i \times 10^{-3}$	M_w^i/M_n^i	W_B	N_w^i	T_m(°C)	T_g^S (°C)	T_g^H (°C)
Z67	6.70	1.7	0.055	169	22	−76	45[b]
Z52	5.19	2.0	0.070	54	17	−75	44[b]
Z20	2.00		0.164	75		−77	38

[a] M_n^i: number-average molecular weight of PTMO segments (polydispersity < 1.15). M_w^i/M_n^i: polydispersity of zwitterionomer. W_B: weight fraction of zwitterionic groups. N_w^i: weight-average degree of chain extension. T_m: melting point. T_g^S: soft phase (matrix) glass transition. T_g^H: hard phase (cluster) glass transition. [b] Broad; observed in DSC thermograms of quenched samples.

aggregates in the previously studied zwitterionomer was shown to be very small, thus making its evolution difficult to follow using normal infrared linear dichroism.[8] PM-IRLD thus constitutes a technique of choice to follow the dynamic orientation and relaxation behavior of the soft and hard regions simultaneously. The results obtained using this technique reveal that the hard zwitterionic domains show a reversal in their orientation direction during the drawing process, analogous to that reported previously for the crystalline hard segments in elastomeric segmented copolymers.[35] This is the first time, to our knowledge, that such a phenomenon has been reported for other than the segmented copolymers.

Experimental Section

Sample Preparation. The zwitterionomers (Scheme 1) were synthesized by B. Grassl in the laboratory of Dr. J.-C. Galin (Institut Charles Sadron, Strasbourg, France), and their structures were characterized by NMR spectroscopy, size exclusion chromatography, thermogravimetric analysis, DSC, etc.[1,2] The PTMO segments, synthesized by cationic polymerization, have a narrow polydispersity index (M_w/M_n) of less than 1.15. Their main characteristics are given in Table 1. SAXS and SANS studies have shown that Z67 and Z52 are characterized by a hexagonal morphology and Z20 by a lamellar morphology.[3]

The zwitterionomers were first cut into small pieces and washed repeatedly in toluene and tetrahydrofuran, which are two sample-swelling solvents, to remove residual components giving rise to a band at about 1700 cm^{-1} in the infrared spectra of the samples. The purified samples were then dissolved in a binary mixture of chloroform and trifluoroethanol (9:1 v/v) at a concentration of 5%. Thin films were prepared by solution casting onto a Teflon film followed by vacuum-drying at 50 °C for about 3 weeks to remove residual solvent (verified by infrared spectroscopy). The sample/Teflon film was cut into strips with a new razor blade, and then the zwitterionomer film was carefully peeled off the substrate in such a way as to avoid inducing orientation. Both ends of the film were wrapped in strips of pyrotape (Aremco) to prevent the sample from slipping between the jaws of the stretcher during deformation. Before stretching, the position of the jaws was manually adjusted so that the film was fully extended. The sample size before stretching was 1 cm in length, 0.8 cm in width, and about 30 μm in thickness.

Orientation Measurements. PM-IRLD spectra were recorded with a Bomen Michelson MB-100 spectrophotometer with the standard transmission optics of this instrument and the two-channel electronic processing described previously.[32] In the interferometer, the intensity of the infrared radiation was first modulated at frequencies $f_i = 2v\bar{\nu}_i$ (between 1 and 8 kHz), where $\bar{\nu}_i$ is the wavenumber of the radiation and v is the velocity of the interferometer moving mirror. The output infrared beam was then polarized with a ZnSe wire-grid polarizer (Specac) and passed through a Hinds PEM-90 type II ZS50 photoelastic modulator, which modulated at 100 kHz ($2f_m$) the polarization of the infrared radiation between the linear parallel and perpendicular states with respect to the stretching direction. After passing through the sample, the doubly modulated infrared radiation was focused with a ZnSe lens onto the photoactive area of either a narrow-band photoconductive MCT detector (Belov Technologies) or a photovoltaic MCT detector (Kolmar Technologies), both cooled at 77 K. The detected signal was then processed by using two dual-channel electronic filters (Stanford Research Systems SR650) and a DSP lock-in amplifier (EG&G 7260DSP), which separated the two components corresponding to the intensity (I_{DC}) and polarization (I_{AC}) modulation. With this technique, the dichroic difference spectrum ($\Delta A = A_{\parallel} - A_{\perp}$) was calculated by using I_{DC}, I_{AC}, and the appropriate calibration procedure.[36]

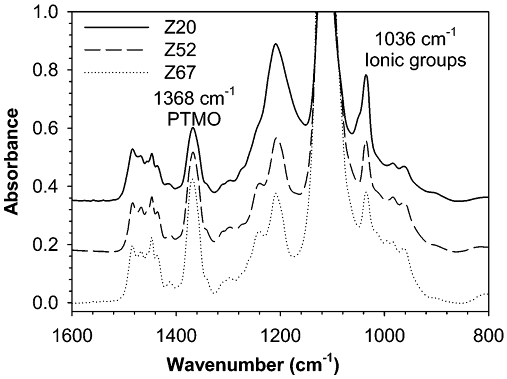


Figure 1. Infrared absorption spectra of the Z67, Z52, and Z20 zwitterionomers.

A homemade stretcher fitted with ZnSe windows was used to stretch the samples to a draw ratio of 3.2 at a draw rate of 2 cm/min. In the standard experiment, a total of 180 spectra of four scans each were recorded with a resolution of 8 cm^{-1} and at a recording rate of ~150 scans/min. For experiments covering a longer relaxation period, additional series of acquisitions (90 spectra of 30 scans, 80 spectra of 75 scans, and 48 spectra of 2750 scans) were obtained. The temperature was controlled by an Omega temperature controller (CN7600) and heating cartridges with an accuracy of ±0.1 °C. A detailed description of the experimental setup can be found elsewhere.[12,32] The experimental conditions (draw rate, temperature, etc.) were selected so as to avoid strain-induced crystallization during deformation.

Because the angle between the transition dipole moment of the vibrations studied and the molecular chain is not known, chain orientation was not calculated directly. Instead, the orientation function of the transition dipole moment was calculated by using the following equation:

$$\langle P_2(\cos\gamma)\rangle = \frac{3\langle\cos^2\gamma\rangle - 1}{2} = \frac{\Delta A}{3A_0}\sqrt{\lambda}$$

where γ is the angle between the transition dipole moment and the stretching direction, A_0 is the initial isotropic absorption, and λ is the draw ratio. In this equation, it is assumed that the sample deformation is homogeneous. The A_0 value was measured before stretching with a Nicolet Magna 560 spectrometer equipped with a MCT detector. The infrared data were processed with Grams 32 software (Thermo Electron) and Microsoft Excel.

Results and Discussion

Figure 1 shows the infrared spectra of Z67, Z52, and Z20. The main bands in the spectrum of Z52 have been assigned in a previous publication.[8] In contrast to Z67

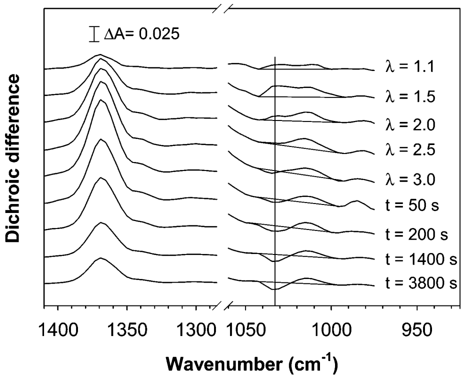


Figure 2. Dichroic difference spectra of Z67 recorded by PM-IRLD during deformation at a rate of 2 cm/min up to a draw ratio of 3.2 and during subsequent relaxation at 40 °C. The draw ratio, λ, during deformation and the relaxation time, t, after the end of deformation are indicated alongside the curves.

and Z52, the spectrum of Z20 shows a small shoulder on the high wavenumber side of the ionic band at 1036 cm^{-1} (SO_3^- symmetric stretch), and the band at about 1200 cm^{-1} (SO_3^- asymmetric stretch) appears to be broader. These differences may be related to the differences in the condensed structure of the polymers (lamellar for Z20, hexagonal for Z52 and Z67) as shown by SAXS and SANS.[3]

The orientation and relaxation behavior was investigated by following the changes in the sulfonate symmetric stretching band at 1036 cm^{-1} and the methylene wagging band at 1368 cm^{-1}, which probe the behavior of the sulfonate groups and the PTMO segments, respectively.[37] A slow stretch rate (2 cm/min) was used to track the orientation variation during the orientation process as fully as possible. A representative example of the changes of the dichroic difference spectra observed during the stretching and subsequent relaxation at constant strain is shown in Figure 2 for Z67 stretched at 40 °C.

The dichroic difference measured for the PTMO band at 1368 cm^{-1} is observed to increase progressively with draw ratio, starting from almost 0 at a draw ratio of 1.1 to its highest value at the end of the deformation. Since the transition moment of the methylene wagging mode is parallel to the main chain, the observation of positive ΔA values for this band indicates that the PTMO chains become progressively oriented along the stretching direction. During the relaxation period, the orientation decreases as a function of time as the chains relax toward an isotropic state.

The 1036 cm^{-1} band associated with the sulfonate groups displays a more complex behavior during deformation. The band first shows increasing positive ΔA values for draw ratios up to about 1.5, and then the dichroic difference decreases and even becomes negative for draw ratios greater than 2.5. Furthermore, the band continues to decrease during the relaxation period. This contrasts not only with the behavior noted for the 1368 cm^{-1} PTMO band but also with that of a weak band located at about 1012 cm^{-1}. This latter band, which is barely visible in the spectra of Figure 1, has been assigned to a skeletal stretching mode of PTMO.[37] As expected for such a vibration, the dichroic difference increases during deformation and decreases during relaxation. The proximity of this band makes a quantitative evaluation of the orientation of the ionic groups using the 1036 cm^{-1} band difficult because the two bands significantly overlap for small draw ratios, and they appear as a derivative-like band for large draw ratios and during relaxation. Nevertheless, the qualitative observations are significant and highly reproducible.

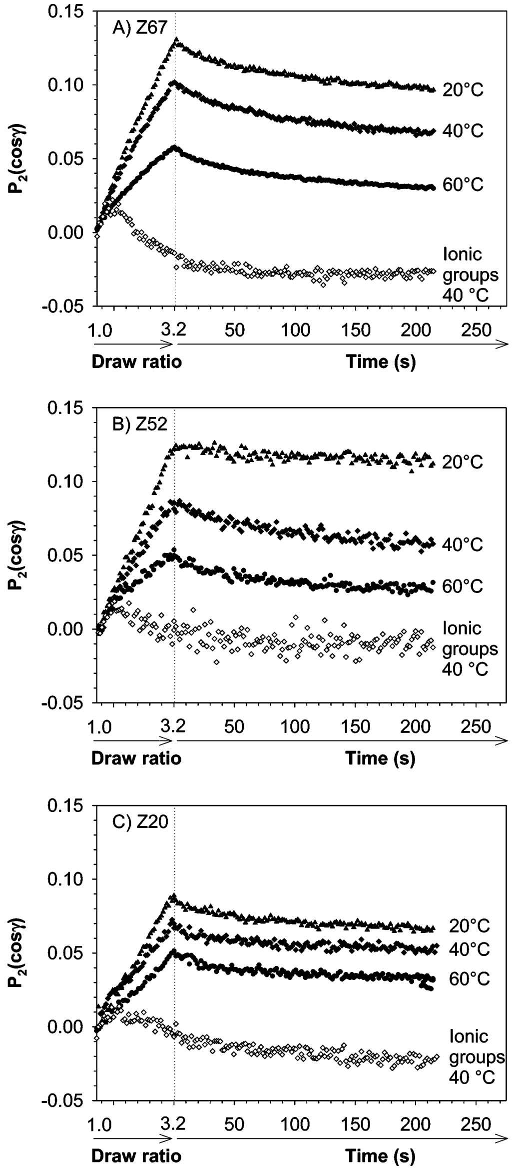
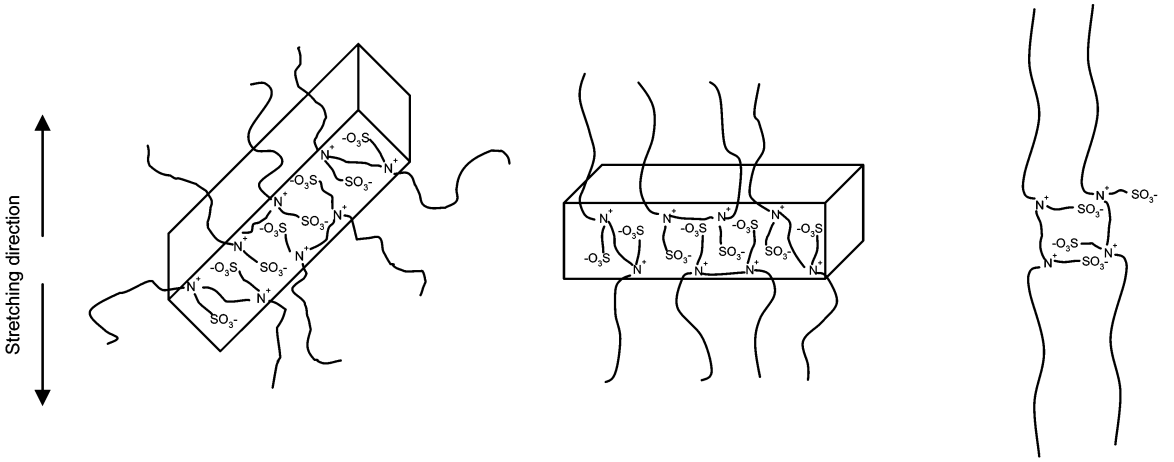


Figure 3. Variations of the orientation function of (A) Z67, (B) Z52, and (C) Z20 during deformation at a rate of 2 cm/min to a draw ratio of 3.2 and during subsequent relaxation, calculated from the 1368 cm^{-1} band at 20 °C (▲), 40 °C (◆), and 60 °C (●) and from the 1036 cm^{-1} band at 40 °C (◇).

The variations of the orientation function of the PTMO segments and the sulfonate groups, calculated from the 1368 and 1036 cm^{-1} bands during stretching and subsequent relaxation at various temperatures, are shown in Figure 3 for Z67 (A), Z52 (B), and Z20 (C). The spectral ranges between 1405 and 1320 cm^{-1} and between 1045 and 995 cm^{-1} were used for the calculation of the orientation function of the bands at 1368 and 1036 cm^{-1}, respectively. For the sake of clarity, the orientation function of the 1036 cm^{-1} band is shown for 40 °C only, since those obtained at 20, 40, and 60 °C are very similar for this time scale. The data show some scattering, especially for the 1036 cm^{-1} band, because each PM-IRLD spectrum was obtained by coadding only four interferograms (in order to have enough time resolution).



$\lambda = 1$
Main axis of ionic domains: isotropic
SO_3^- sym. stretch axis: isotropic
PTMO segments: isotropic

$\lambda \sim 1.5$
Main axis of ionic domains: perpendicular
SO_3^- sym. stretch axis: parallel
PTMO segments: parallel

$\lambda > 1.5$
Small aggregates (ion pairs, quartets…)
SO_3^- sym. stretch axis: perpendicular
PTMO segments: parallel with potential crystallization

Figure 4. Model showing the effect of stretching on the orientation of lamellar- or cylinder-like zwitterionic domains and hence on the orientation of the side chains. The orientations given are with respect to the stretch direction. The detailed arrangements shown for the zwitterionic moieties (disposition of ions with respect to one another, conformation of aliphatic spacers) are for illustrative purposes only and are not necessarily to be taken literally.

Figure 3 shows that, for all three zwitterionomers (and for all three temperatures), the orientation function of the PTMO segments increases continuously in the stretching direction during the orientation process, whereas that of the sulfonate groups displays more complex behavior (as was observed qualitatively in Figure 2). The latter clearly increases only at the beginning of the orientation process (to reach a maximum of $\approx$0.015 at a draw ratio of about 1.5), and then it decreases to become negative before the end of the stretching process. In the subsequent relaxation period at the constant draw ratio of 3.2, the orientation function for the sulfonate groups continues to decrease slightly for some time. The PTMO segments show moderate relaxation in the time scale shown.

The above orientation and relaxation behavior may be compared to analogous behavior that was observed previously for semicrystalline segmented copolymers characterized by a crystalline hard phase and an elastomeric soft phase.[21−23,35,38] In these copolymers, the soft domains likewise display a monotonic increase in orientation with draw ratio, whereas the orientation function of the hard domains initially decreases, giving negative values, and then increases and becomes positive. The initial decrease was attributed to the orientation of the long dimension of the crystalline lamellae in the stretch direction, which results in a transverse orientation for the polymer backbone. The turnaround at higher elongations was attributed to a breakdown of the original crystallites into smaller fragments with reorientation of the hard segment chains parallel to the stretch direction (although other mechanisms may also be operative[35]). This phenomenon was not observed in segmented elastomeric copolymers with a glassy hard phase.[23]

In the case of the present zwitterionomers, the complex orientation behavior of the sulfonate groups may be related to the anisotropic shapes of the ionic domains, which, as mentioned above, are lamellar for Z20 and cylindrical for Z52 and Z67. This anisotropy of the ionic domains is thus analogous to that of the lamellar crystalline domains. Accordingly, the orientation and relaxation behavior of the zwitterionomers might be rationalized by a mechanism analogous to that for the semicrystalline copolymers. It can be assumed that, before deformation, the ionic domains of either lamellar or hexagonal morphology are randomly oriented throughout the sample. Upon deformation, the flexible PTMO chains in the soft phase orient along the stretch direction and transmit the stress to the ionic domains, which can then rotate as anisotropic rigid entities. The resulting positive dichroism of the sulfonate group means that its transition moment dipole tends to orient parallel to the stretch direction. If the zwitterionic lamellae or cylinders are formed as represented schematically in Figure 4, stretching of the PTMO chains clearly must cause the long axis of the rigid entities to orient on average perpendicular to the stretch direction, which results in the sulfonate groups orienting parallel to the stretch direction, consistent with the experimental observation. This is also in agreement with results of Grassl,[39] who used SANS and SAXS to study the deformation of similar (alkoxydicyanoethenolate-based) zwitterionomers and found that the initially isotropic lamellae and cylinders orient with their long axis perpendicular to the stretching direction upon uniaxial deformation. It should be noted in this discussion that, although the focus is on the zwitterionic domains, these domains probably should include the immediate PTMO region, whose mobility is expected to be reduced by the ionic cores (in accordance with the Eisenberg−Hird−Moore model for ionomers[4]).

The decrease in orientation of the sulfonate groups for draw ratios beyond about 1.5 can be rationalized by a progressive disruption of the ionic domains in response to the applied stress and deformation, possibly giving isolated zwitterions or lower-order ionic aggregates such as zwitterionic pairs, quartets, etc. (as suggested in Figure 4). This disruption should be accompanied by a reorientation of the "freed" main chain segments along the stretch direction. Under these circumstances, the sulfonate groups that are at the ends of the side-chain moieties, which should reorient more or less perpendicularly to the main-chain segments to which they are

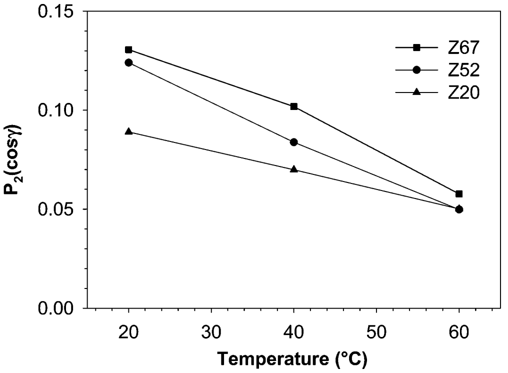


Figure 5. Effect of temperature on the orientation function calculated from the band at 1368 cm^{-1} at the end of the deformation for samples of Z67, Z52, and Z20 stretched at a rate of 2 cm/min to a draw ratio of 3.2.

attached, may be expected to now have their transition moment dipole perpendicular to the stretch direction (see Figure 4), resulting in a negative orientation function. Of course, this reorientation is not instantaneous, nor does the disruption of all ionic domains occur simultaneously, explaining why the reorientation occurs over a lengthy period during the latter part of the deformation process and continues for some time during the subsequent relaxation at constant draw ratio.

It is of interest to compare the orientation of the PTMO segments at the different zwitterion contents and the different temperatures. The orientation achieved at maximum deformation ($\lambda = 3.2$) and before subsequent relaxation (determined from Figure 3) is plotted in Figure 5. The magnitude of the orientation function is observed to decrease with temperature, an effect that is generally associated with increased molecular mobility as the temperature is raised. Figure 5 also shows that the ionic aggregates do not behave as permanent cross-link points; that is, they do not prevent some flow of the PTMO chains. The rate of decrease in orientation with temperature is greater for Z67 and Z52 than for Z20. More specifically, the PTMO orientation in Z20 is significantly less than that in Z67 and Z52 at ambient temperature, whereas all three zwitterionomers show similar PTMO orientation at 60 °C. (This observation remains true also after 200 s of relaxation, i.e., near the end of the relaxation period shown in Figure 3.) This contrasts with what was observed in polystyrene-based statistical ionomers, where the polystyrene orientation increases with ion content,[17] and with what would be expected if the ionic aggregates act as effective cross-links.[13,14]

Part of the explanation for these observations may lie with the difference in morphology of the aggregates (lamellar for Z20 and cylindrical for Z52 and Z67) or with differences in their sizes or coherence domains, which are not known. The hard-phase glass transition temperature, which is broad and which occurs at similar temperatures for all three zwitterionomers (see Table 1), cannot be responsible for the differences in orientation behavior. On the other hand, a significant difference in the fraction of the hard phase (or so-called cluster phase)[4-6] can also contribute to the observations summarized in Figure 5. In particular, Z20 has been shown, by dynamic mechanical thermal analysis (DMTA), to have a fairly large cluster transition area, suggesting a relatively large hard-phase fraction, whereas this transition is essentially undetectable by DMTA for Z52 and Z67.[40] Now, when the PTMO orientation is measured, it gives the average for all of the PTMO in both the soft and hard phases. However, it is unlikely that the PTMO in the hard phase will undergo as much orientation as that in the soft phase at 20 °C, which is below the hard phase T_g. This means that the observed PTMO orientation for Z20 must be significantly less than the real orientation of the PTMO that is located in the soft phase of this sample, whereas for Z67 and Z52, which have a much smaller hard phase fraction, the observed PTMO orientation should be much closer to the real PTMO orientation in the soft phase. At 60 °C, where the hard phase has softened, this effect is much less operative, if at all. At these higher temperatures, one may expect significant ion hopping to occur and contribute greatly to chain relaxation.

Interestingly, DMTA experiments,[40] in which low strains are applied, have indicated that Z67 and Z52 behave similarly to covalent elastomers up to at least 100 °C (with the moduli increasing somewhat with increasing temperature), indicating little or no ion hopping. This apparent contradiction with the present results may be related to the orientation mechanism involving the sulfonate groups as proposed above. That is, it is reasonable to presume that the elastomeric properties of the two zwitterionomers are retained as long as the disruption of the hard domains has not taken place, that is, for low draw ratios (e.g., below 1.5, where DMTA experiments are generally performed), and that irreversible permanent plastic flow only occurs at higher draw ratios, where there is disruption of the hard domains. On the other hand and in contrast to Z67 and Z52, the DMTA modulus of Z20 begins to decrease with increasing temperature soon after the soft phase glass transition. This may be rationalized by ion hopping and some reorganization occurring at low strain without disruption of the overall lamellar structure, made possible by the greater proximity of the ionic groups and neighboring lamellae in this higher ion content zwitterionomer. If ion hopping occurs in Z20 even at low strains (above the PTMO glass transition), it must also be present at the high strains of the present experiments at 20 °C and probably to a significantly greater extent than for Z52 and Z67. This is therefore another possible contributor to the differences in the orientation behavior of the three zwitterionomers.

A final contribution to consider is that the first few TMO repeat units attached to the rigid zwitterionic domains have a preferred orientation relative to these domains, which may well be at some angle given the bond directions around the nitrogen cation, in particular at 20 °C. When the domains are reoriented perpendicular to the stretch direction, as depicted in Figure 4, these segments would be preferentially oriented away from the stretch direction and thus contribute to a reduction of the PTMO orientation. This reduction would again be greater in Z20 than in Z52 and Z67, since the relative amount of PTMO units vicinal to the ionic domains is greater in the former compared to the latter. Nevertheless, this effect may be expected to be relatively weak since the number of TMO units affected is small compared to the PTMO segment lengths.

A last experiment was performed to observe the relaxation behavior up to much longer times. Figure 6 shows the orientation relaxation curves obtained from the 1036 and 1368 cm^{-1} bands recorded for 15 h for Z67 deformed at 20 and at 60 °C. When the deformation is performed at 60 °C, the orientation function calculated

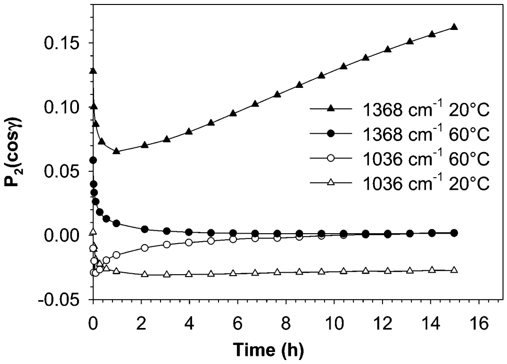


Figure 6. Changes of the orientation function calculated from the 1036 and 1368 cm^{-1} bands during the relaxation of Z67 at 20 and 60 °C following deformation at a rate of 2 cm/min to a draw ratio of 3.2. The symbols are used for identification only and do not represent the actual data spacing (see Experimental Section).

from the 1368 cm^{-1} PTMO band decreases gradually with time to almost zero, indicating that the sample has reached an essentially isotropic state. In contrast, when the deformation is performed at 20 °C, the PTMO orientation function decreases for about an hour but then it starts increasing again, reaching values at the end of the relaxation period that are even larger than those at the end of the deformation period. This phenomenon was also observed for initially amorphous poly(ethylene terephthalate) and was ascribed to a stress-induced crystallization that occurred during relaxation.[41] The increase in orientation was attributed to some fraction of amorphous disordered chains being transformed into a highly oriented crystalline structure. That similar stress-induced crystallization of the PTMO chains occurs during relaxation of Z67 is supported by spectral changes that occur during the orientation increase starting at about 270 s, for example, by the appearance of the crystalline methylene wagging deformation at 1371 cm^{-1} (shifted from the amorphous band at 1368 cm^{-1}) and of the symmetric COC stretching band at 997 cm^{-1}.[8] The amount of crystallization involved is low (judging qualitatively from the spectral changes and based on the analysis of ref 8).

As observed in Figure 3, the orientation of the 1036 cm^{-1} sulfonate absorption band becomes increasingly negative during the early part of the relaxation, whether deformation is performed at 20 or 60 °C. For deformation at 60 °C, this orientation reaches a maximum negative value after about 175 s and then "relaxes" with time until the sample is isotropic. In contrast, at 20 °C, the orientation reaches its maximum negative value more than an hour after deformation and then remains more or less constant. These results are in agreement with the model proposed above. When no crystallization occurs, i.e., at 60 °C, the perpendicular orientation of the sulfonate groups is driven by the disruption of the ionic aggregates and reorientation of the side chains. Since the PTMO main chain of the polymer relaxes to the isotropic state with time, it is to be expected that the side chains do likewise, as observed in Figure 6. On the other hand, crystallization has the effect of locking the PTMO chains in an oriented state and thus prevents relaxation of the side chains, as observed at 20 °C.

Conclusions

The orientation and relaxation behavior of regularly segmented zwitterionomers with PTMO blocks of different lengths was investigated at temperatures much higher than the T_g of the PTMO matrix. PM-IRLD was shown to be a very useful technique for such studies because of its high sensitivity and good time resolution. It was found that the orientation of the PTMO segments increases continuously with draw ratio during deformation and decreases as a function of time toward the isotropic state during relaxation, as would be expected. In contrast, the orientation and relaxation behavior of the ionic aggregates is more complex. For all three zwitterionomers and at all three temperatures studied, the orientation function of the sulfonate groups increases only at the beginning of the orientation process, to reach a maximum of 0.015 at a draw ratio of about 1.5, and then it decreases to become negative before the end of the stretching period. It continues to decrease for some time during the relaxation period. These results suggest that, up to a draw ratio of about 1.5, the stress due to the orientation of the PTMO chains along the stretch direction induces orientation of the ionic domains (which act as anisotropic rigid entities) perpendicular to the stretch direction, which corresponds to the ionic side chains being parallel to the stretch direction. Beyond a draw ratio of about 1.5, the applied stress appears to cause the progressive disruption of the ionic aggregates accompanied by a reorientation of the "freed" side chain segments perpendicular to the stretch direction. It was also noted that stress-induced crystallization of the PTMO chains could be observed for Z67 during relaxation over a long period of time (hours instead of minutes) at ambient temperature and that this locks in the negative orientation of the ionic side chains.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fonds Québécois de Recherche sur la Nature et les Technologies (FQRNT) is acknowledged. We are grateful to Drs. J.-C. Galin and B. Grassl for their generous gift of the zwitterionomers.

References and Notes

(1) Grassl, B.; Galin, J.-C. *Macromolecules* **1995**, *28*, 7035.
(2) Grassl, B.; Meurer, B.; Scheer, M.; Galin, J.-C. *Macromolecules* **1997**, *30*, 236.
(3) Grassl, B.; Mathis, A.; Rawiso, M.; Galin, J.-C. *Macromolecules* **1997**, *30*, 2075.
(4) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(5) Eisenberg, A., Kim, J.-S., Eds. *Introduction to Ionomers;* John Wiley & Sons: New York, 1998.
(6) Tant, M. R., Mauritz, K. A., Wilkes, G. L., Eds.; *Ionomers: Synthesis, Structure, Properties, and Application;* Blackie Academic and Professional (Chapman & Hall): New York, 1997.
(7) Ehrmann, M.; Mathis, A.; Meurer, B.; Scheer, M.; Galin, J.-C. *Macromolecules* **1992**, *25*, 2253.
(8) Wang, Y.; Bazuin, C. G.; Pézolet, M. *Macromolecules* **2001**, *34*, 6344.
(9) Tassin, J. F.; Monnerie, L.; Fetters, L. J. *Macromolecules* **1988**, *21*, 2404.
(10) Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. *Macromolecules* **1989**, *22*, 1334.
(11) Siesler, H. W.; Hayes, C.; Bokobza, L.; Monnerie, L. *Macromol. Rapid Commun.* **1994**, *15*, 467.
(12) Pellerin, C.; Prud'homme, R. E.; Pézolet, M. *Macromolecules* **2000**, *33*, 7009.
(13) Mott, P. H.; Rizos, A.; Roland, C. M. *Macromolecules* **2001**, *34*, 4476.
(14) Kajiyama, T.; Stein, R. S.; MacKnight, W. J. *J. Appl. Phys.* **1970**, *41*, 4361.
(15) Kajiyama, T.; Oda, T.; Stein, R. S.; MacKnight, W. J. *Macromolecules* **1971**, *4*, 198.

(16) Uemura, Y.; Stein, R. S.; MacKnight, W. J. *Macromolecules* **1971**, *4*, 490.
(17) Fan, X.-D.; Bazuin, C. G. *Macromolecules* **1993**, *26*, 2508.
(18) Bazuin, G. C.; Fan, X.-D.; Lepilleur, C.; Prud'homme, R. E. *Macromolecules* **1995**, *28*, 897.
(19) Bazuin, C. G.; Fan, X.-D. *Macromolecules* **1998**, *31*, 1321.
(20) Ma, X.; Sauer, J. A.; Hara, M. *Macromolecules* **1995**, *28*, 5526.
(21) Kimura, I.; Ishihara, H.; Ono, H.; Yoshihara, N.; Nomura, S.; Kawai, H. *Macromolecules* **1974**, *7*, 355.
(22) Lilaonitkul, A.; West, J. C.; Cooper, S. L. *J. Macromol. Sci., Phys.* **1976**, *B12*, 563.
(23) West, J. C.; Cooper, S. L. *J. Polym. Sci., Polym. Symp.* **1977**, *60*, 127.
(24) Ward, I. M. *Structure and Properties of Oriented Polymers,* 2nd ed.; Chapman & Hall: London, 1997.
(25) Spontak, R. J.; Vratsanos, M. S. *Macromolecules* **2000**, *33*, 2290.
(26) Aoki, Y.; Hatano, A.; Tanaka, T.; Watanabe, H. *Macromolecules* **2001**, *34*, 3100.
(27) Pellerin, C.; Prud'homme, R. E.; Pézolet, M. *Polymer* **2003**, *44*, 3291.
(28) Hipps, K. W.; Grosby, G. A. *J. Phys. Chem.* **1979**, *83*, 555.
(29) Drake, A. F. *J. Phys. E: Sci. Instrum.* **1986**, *19*, 170.
(30) Nafie, L. A.; Vidrine, D. W. Double Modulation Fourier Transform Spectroscopy. In *Fourier Transform Infrared Spectroscopy*; Ferraro, J. R., Basile, L. J., Eds.; Academic Press: New York, 1982; Vol. 3, p 83.
(31) Nafie, L. A. Polarization Modulation FTIR Spectroscopy. In *Advances in Applied Fourier Transform Infrared Spectroscopy*; Mackenzie, M. W., Ed.; John Wiley & Sons Ltd.: New York, 1988; Vol. 3, p 68.
(32) Buffeteau, T.; Pézolet, M. *Appl. Spectrosc.* **1996**, *50*, 948.
(33) Buffeteau, T.; Pézolet, M. Linear Dichroism in Infrared Spectroscopy. In *Handbook of Vibrational Spectroscopy*; Griffiths, P. R., Chalmers, J. M., Eds.; John Wiley & Sons: Chichester, 2001; Vol. 1.
(34) Buffeteau, T.; Natansohn, A.; Rochon, P.; Pézolet, M. *Macromolecules* **1996**, *29*, 8783.
(35) Yeh, F.; Hsiao, B. S.; Sauer, B. B.; Michel, S.; Siesler, H. W. *Macromolecules* **2003**, *36*, 1940.
(36) Buffeteau, T.; Desbat, B.; Pézolet, M.; Turlet, J. M. *J. Chim. Phys. Phys.-Chim. Biol.* **1993**, *90*, 1467.
(37) Imada, K.; Miyakawa, T.; Chatani, Y.; Tadokoro, H.; Murahashi, S. *Makromol. Chem.* **1963**, *83*, 113.
(38) McLean, R. S.; Sauer, B. B. *J. Polym. Sci., Part B* **1999**, *37*, 859.
(39) Grassl, B. Ph.D. Thesis, Université Louis Pasteur, Strasbourg, 1995.
(40) Vuillaume, P. Y. M.Sc. Thesis, Université Laval, Québec, 1996. Vuillaume, P. Y.; Grassl, B.; Galin, J.-C.; Bazuin, C. G., to be published.
(41) Duchesne, C.; Kong, X. H.; Brisson, J.; Pézolet, M.; Prud'homme, R. E. *Macromolecules* **2002**, *35*, 8768.

MA047330E