End-Group Effect on Chain Conformation of Poly(propylene glycol) and Poly(ethylene glycol)

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ABSTRACT: A comparison is made of the chain conformational distribution of hydroxy-terminated poly(propylene glycol)(PPG) and poly(ethylene glycol)(PEG) with their methoxy-terminated derivatives. The significant end-group dependence on the glass transition temperature in PPG was observed by differential scanning calorimetry. Raman active skeletal vibrations in the low-frequency region indicated a significant difference in chain conformation distribution between methoxy- and hydroxy-terminated PPGs, yet almost no difference between MPEG and HPEG. The increased chain stiffness in HPPG in comparison to MPPG has been attributed to the hydrogen-bonding interaction associated with the hydroxy end group in HPPG. Furthermore, the structural differences observed between PPG and PEG have been attributed to the differences in the interaction of the hydroxy end group to the ether oxygen in the two polymers. The interaction between the hydroxy end group and ether oxygen differs because the —CH_3 side group is present for one and not for the other. These structural differences are reflected in the glass transitions temperatures measured. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 197–202, 1997

INTRODUCTION

Polymeric electrolytes, particularly polyether–inorganic salt complexes, have been extensively studied because of their potential in commercial applications such as batteries as solid electrolytes.[1,2] In those systems, it is known that the ion-transport mechanism is intimately related to the polymer structure. Therefore, numerous studies of polyether-based polymeric electrolytes were focused on the elucidation of the polyether backbone structure and dynamics. In previous studies, we observed that end groups in linear systems, and junction points in the case of networks, can perturb the chain conformation distribution of poly (propylene glycol) (PPG)-based polymeric electrolytes.[3–5] In addition, the size, number, and chemical moiety of these specific functional groups critically determine the transport properties of the polymeric electrolytes.[3–5] From spectroscopic evidence, we also established that the end groups/junction points are critical in the determination of the chain conformational distribution of these polymeric electrolytes. In earlier studies, it was also shown that in the presence of $LiClO_4$ macroscopic phase separation occurs for methoxy-terminated PPG (MPPG) while salt-complexed hydroxy-terminated PPG (HPPG) of all molecular weights form homogeneous mixtures. Our analysis indicated that hydroxy end groups play a significant role in salt–polymer complex formation and chain conformational distribution.[3–5] The exact relationship between chain conformation distribution to the transport property is not well defined. In this study, we aimed to understand better the chain conformation as a function of the chemical moiety of the end groups. Presumably, chain conformation distributions have different chain dynamics, thus affecting the ionic mobility of these polymeric electrolytes.

The molecular weight dependence associated with the structural relaxation behavior of oligomeric HPPG has been previously examined.[6] Sound velocity and Raman spectroscopy were used to determine the effects of end-group interaction on electrolyte structure. The increase in sound velocity for samples with decreasing molecular weight was attributed to the decrease in chain flexibility. This stiffening was assigned to the relative increase in the number of end groups for samples of decreasing molecular weight. End groups play an extremely important role because of possible strong intermolecular interactions between hydroxyl units and ether oxygen along the chain. For those polyethers, an intense Raman active vibration assignable to the disordered longitudinal acoustic mode (D-LAM) was observed in the $200-300$ cm^{-1} region.[6] Based on the observed frequency–molecular weight relationship, alteration of chain conformation distribution can result from these interactions or the presence of ions.[3-6] Based on normal vibrational analysis or a continuum model, the frequency of LAM is known to be related to the single-chain density and elastic modulus.[7-10] The relationship between D-LAM frequency and chain structure, however, is much less straightforward.[7-11] This low-frequency vibration is, however, unquestionably highly dependent on molecular weight and highly sensitive to structural changes associated with polyethers forming electrolytes.

In this study, we reexamined end-group effects on the conformation of PPG by comparing the effects of end groups on the structure of HPPG and MPPG as a function of molecular weight. In addition, end-group effects in PEG were studied by comparing HPEG and MPEG. These two types of polyethers behave quite differently in their interactions with counterions. By studying the end-group effects on PPG and PEG, it is also possible to deduce the effects of —CH$_3$ side groups in chain conformations of PPG. Differential scanning calorimetry (DSC) and Fourier transform Raman spectroscopic studies were utilized for this purpose. DSC was used to measure the glass transition temperature which reflects chain segmental mobility. Raman active vibrational bands in the low-frequency region, $200-300$ cm^{-1}, have been known to represent skeletal bending vibrational modes of chain backbones. These frequencies and vibrational bandwidths are known to be dependent on chain conformational distribution. The band in this region has been assigned to the disordered longitudinal acoustic mode (D-LAM).[7-11]

The band position and change in D-LAM indirectly reflects the change in chain flexibility. In this study, we used the changes in this band observed for various model polymers to characterize chain conformation differences and thus to clarify the differences observed in the glass transition temperature and macroscopic transport property.

EXPERIMENTAL

Hydroxy-terminated poly(propylene glycol) (HPPG), poly(ethylene glycol) (HPEG), and methoxy-terminated poly(ethylene glycol) (MPEG) were obtained from Aldrich Chemical and Fluka Chemical Co. Methoxy-terminated PPG (MPPG) of molecular weights 425 and 1000 was prepared by treating HPPG first with NaH and then with CH$_3$I under dry argon gas. The detailed procedure was described in our previous study.[3-5] Isotactic PPG (IsoPPG) of molecular weight M_n 710 ($M_w/M_n = 1.3$) was synthesized by Dr. Dorman of Dow Chemical Co. IsoPPG has hydroxy groups at the ends. The stereoregularity of this model polymer was determined as 95% isotactic and the regioselectivity is 80% of the head-to-tail. All samples were dried with extreme precaution to prevent water contamination during sample preparation.

Dispersive Raman spectra were obtained with an ISA Model U1000 Raman spectrometer equipped with a Spectra Physics Model 165-08 argon ion laser as the excitation source. The excitation wavelength of the argon laser line was 514.5 nm. This instrument can provide extremely accurate polarization characteristics of Raman active bands. A Newport Model RSA-2 polarizer was used as an analyzer in the polarized Raman spectroscopy. The power at the sample was 100 mW; scattered light was detected by a cooled photomultiplier. Data points were collected every 0.25 cm^{-1}. The time of measurement at each point was 3 s. Bandpass was maintained at 1.25 cm^{-1}. Dispersive Raman data were difficult to obtain for other samples since some exhibit fluorescence when excited with laser excitation in the visible region. This difficulty was overcome by the use of a long wavelength excitation associated with Fourier transform Raman spectroscopy. These spectra were obtained at room temperature using a Bruker FRA 106 spectrometer. A Nd:Yag laser (wave length: 1064 nm) was used as the excitation. Laser output power was maintained at 500 mW. To obtain a good signal-to-noise ratio for analysis, 1024 scans were coadded. The excitation
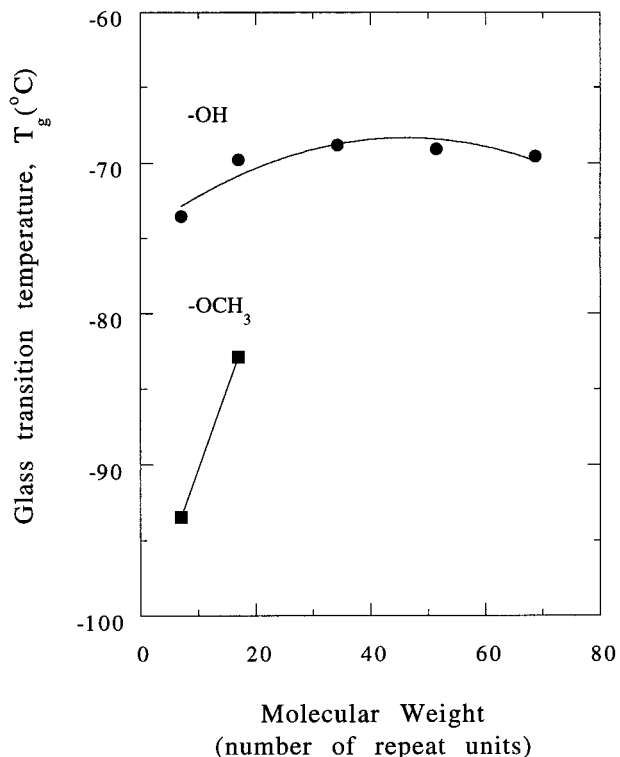
Figure 1 Glass transitions temperatures measured for PPGs of two different types of end groups.

collection geometry was 180° and spectral resolution was maintained at 4 cm^{-1}.

Differential scanning calorimetry (DSC) was performed with a DuPont 2910 Model. Data were collected from -150°C to room temperature at a 20°C/min heating rate under a N$_2$ purge. The instrument was calibrated at -87 and 156.6°C by cyclohexane and indium. Samples for DSC measurements were prepared in a glove box under an argon gas stream and transferred to the DSC sample cell in the dessicator. Glass transition temperatures were determined at inflection points of the step change in the thermograms. The glass transition temperatures observed for a number of polyethers by changing molecular weight and end groups are shown in Figure 1.

RESULTS AND DISCUSSION

The glass transition temperatures for the two types of PPGs shown in Figure 1 are extremely interesting. The transition temperatures measured are high considering the molecular weights of the samples studied. The most unusual aspect is that there is no measurable/interpretable mo-

lecular weight dependence on the glass transition temperature for HPPGs for all the samples of varying molecular weight. This is unusual since it has already been established that glass transition temperature is dependent on polymer molecular weight below a degree of polymerization of several hundred.[12] Although we have only two data points for MPPGs, significant molecular weight dependence on the glass transition temperature is observed by removing hydroxy end groups and replacing them with methoxy groups. By changing hydroxy to methoxy groups, the glass transition temperature was decreased by 20°C for molecular weight 425 and by 12°C for 1000. The only difference between the two types of polyethers is the possible intermolecular interactions associated with hydroxy end groups. These interactions can be significant because the hydrogen bonds formed between hydroxy groups or to ether oxygen can be extremely strong. The increase in transition temperatures associated with hydroxyl-terminated samples in comparison to the methoxy-terminated samples can be explained by the network formation either due to the end-to-end hydrogen-bonding interaction or the physical network formation by interaction between hydroxy groups and ether oxygen. Of more interest and more difficult to explain is the lack of molecular weight dependence for the samples studied.

Although a detailed explanation for the spectroscopic features has yet to be provided, there is no doubt that the low-lying vibrations are indeed sensitive to the structure of the polyethers studied. For both PPGs and PEGs, strong vibrations exist in the 200–300 cm^{-1} region. The spectra in the 100–400 cm^{-1} region obtained for the series of samples [425(HPPG425), 1000(HPPG1000), 2000(HPPG2000), 3000(HPPG3000), and 4000 (HPPG4000)] are shown in Figure 2. The band in the 200–300 cm^{-1} region shifts to lower frequencies as the molecular weight of HPPG increases. This broad strong vibration is, in fact, a doublet, making it difficult to define band frequencies due to their broad features. To characterize the bands in this region, the polarization experiment was undertaken with use of a dispersive Raman spectrometer. The depolarized (perpendicularly [⊥]) and polarized (parallel [∥]) spectra obtained for HPPG1000 are shown in Figure 3. There is no question that the bands in the low-frequency region are all completely polarized, consistent with the assignments being D-LAM in nature.[9] It is known that when assigned unambigu-
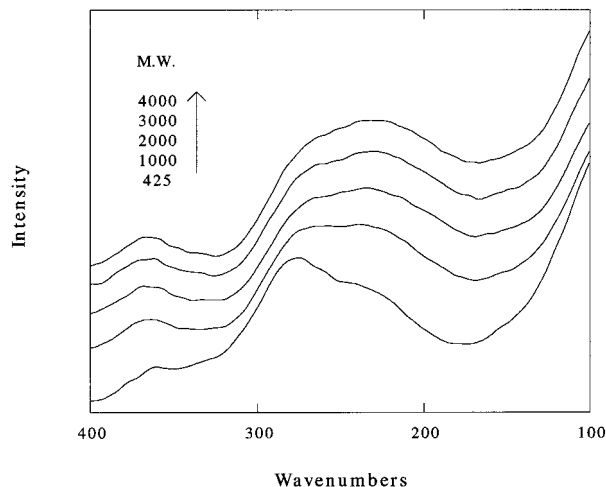
Figure 2 Low-frequency Raman spectra obtained for hydroxyl-terminated PPGs of various molecular weight.

Figure 4 Low-frequency Raman data obtained for hydroxy- and methoxy-terminated PPGs.

ously D-LAMs should have low depolarization ratios.[9]

The vibrational bands in this region usually represent a skeletal bending mode. The D-LAM band frequency has also been known to be inversely proportional to the square of n, the number of skeletal atoms in the chain for n-alkane systems.[8] It has been suggested previously that these bands observed for PPG are indeed D-LAM.[6] The assignment was based on the fact that the central frequency of the broad profile was proportional to $1/n^2$. As can be seen in Figures 2 and 3, the bands in this region are quite complex, mak-
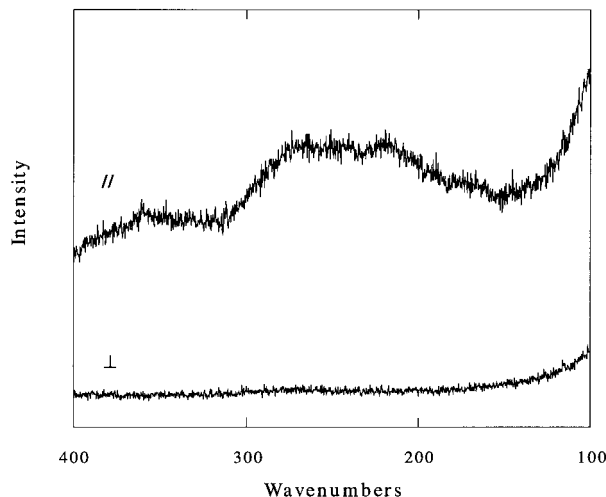

Figure 3 Polarized and depolarized Raman spectra obtained for hydroxy-terminated PPG. The molecular weight is 1000.
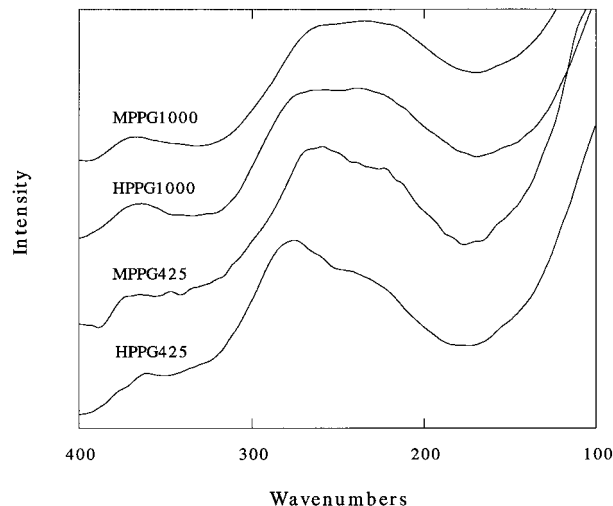
ing quantitative analysis difficult. Nevertheless, the features observed can serve as an analytical probe showing the differences associated with various samples. Instead of seeing one vibration in every spectrum obtained, the broad band in each case can be deconvoluted into a doublet. The apparent shift in frequency as a function of molecular weight may be associated with a relative intensity change of the components. For HPPGs, the lower component increases in intensity as a function of molecular weight. As it is extremely difficult to determine band frequencies for each component of the doublet above molecular weight 1000, we could not estimate molecular weight dependence of the frequency. However, it is unlikely to follow the relationship obtained for n-alkanes.[8] The rotational potential around the individual backbones should not change as a function of molecular weight. Therefore, the change of the relative intensity of these two components as well as the frequency shift can only be explained by the different relative amount of hydroxy groups for samples of varying molecular weights.

Raman spectra obtained for MPPG and HPPG (molecular weight 425 and 1000) are shown in Figure 4. The higher-frequency component of the doublet was observed at 275 and 258 cm^{-1} for the HPPG425 and HPPG1000, respectively. The frequency shifts for the two components are difficult to evaluate quantitatively. These two components may very well be changing their positions separately or together. The apparent change in positions can also be associated with the relative intensity change. Nevertheless, the 17 cm^{-1} dif-
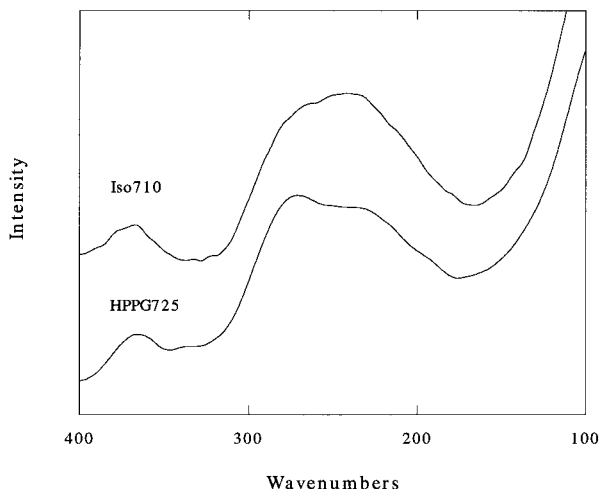
Figure 5 Low-frequency Raman spectra obtained for atactic and isotactic PPG.

ference between the central component of the composite band of HPPG425 and HPPG1000 was reduced to ~ 5 cm^{-1} between MPPG425 and MPPG1000. The band shift to lower frequency can be interpreted to be associated with an increase in chain flexibility or a different conformational distribution. The higher frequencies of these components of low molecular weight samples are consistent with DSC results. The higher concentration of hydroxy groups in lower molecular weight samples induced a higher frequency of the composite bands. The relative intensity of the two bands deserve further analysis.

It is clear that the multicomponent feature of this band in the low-frequency region still exists for MPPGs as seen in Figure 4. Therefore, the relative intensity change with change in molecular weight of HPPG was not caused directly by differences in the relative content of hydroxy end groups which can result in the change in chain conformational distribution and then the shape and frequency of D-LAM bands. The relative intensity of the doublet is not due to polydispersity of the samples used. Our samples actually have a fairly low molecular weight distribution (M_w/M_n = 1.06). To assess whether the molecular weight dependence of the doublet is related to chain configuration, we compared atactic HPPG (HPPG) with isotactic HPPG (IsoPPG). The Raman spectra of HPPG and IsoPPG of molecular weight $\sim$ 700 are shown in Figure 5. The relative intensity of the lower-frequency side increased in IsoPPG in comparison to HPPG. Therefore, the relative intensity of the doublet of the bands can be, in part, attributed to the tacticity distribution de-

pending on the molecular weight of PPG. However, the structure for all the atactic HPPGs studied are uniform.[13,14] At this moment, we wish only to point out that the molecular weight dependence of the apparent band position in the D-LAM region for the atactic PPG samples are related to the number of end groups. The relative intensity is not significantly perturbed by the presence of end groups. We suggest that the complexity of the bands in this region is related to the intrinsic properties of the chains.

For comparison with PPG, the Raman spectra of HPEG and MPEG for molecular weight 400 are shown in Figure 6. The bands in the region shown undoubtedly are assignable to skeletal bending vibrations, accounting for the similarity in the characteristics observed for PPG and PEG systems independent of slight differences in structural detail. As seen in Figure 6, spectral differences in the 200–300 cm^{-1} region by changing the PEG end group from —OH to —OCH$_3$ were negligible in comparison to the significant changes observed for PPG samples. In fact, the band frequency at maximum intensity in this region for MPEG400 was found to be 3 cm^{-1} higher than that of HPEG400, in contrast with end-group effects found in PPG.

A model to account for the differences in the spectroscopic features and thermal data observed for HPPG and HPEG systems has yet to be developed. A possible explanation may be the strong hydrogen bonds along the chain between the end groups and ether oxygen. If the spectral change shown in PPG after changing the end group was due only to the hydrogen-bonding interaction be-
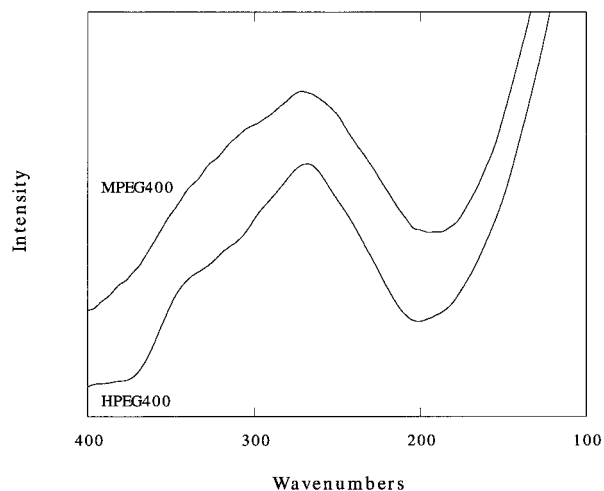

Figure 6 Low-frequency Raman spectra obtained for hydroxy- and methoxy-terminated PEG.

tween hydroxy end groups, similar changes should be observed in PEG, contrary to our observations (Fig. 6). The presence of methyl groups in PPG are known to affect the type and magnitude of interactions between the ether oxygen and hydroxyl end groups.[3–5] Spectroscopic observations indicate that the interaction of the hydroxy group to the ether oxygen in PPGs affect the chain conformational distribution, which, in turn, may affect the chain dynamics as observed in the differences in thermal data. The interaction between hydroxyl groups and ether oxygen in PEG are difficult to evaluate. Earlier studies demonstrated the effects of end–end interactions in the crystalline state.[15] No quantitative analysis of the physical networks formed by intermolecular interactions between end groups and ether oxygen along the chain is available. The situation is also complicated because it is extremely difficult to measure the glass transition temperatures of PEGs because of their propensity for crystallization.

CONCLUSIONS

Based on Raman active spectroscopic features (skeletal bending vibrations) found in the extremely low-frequency region ($200–300$ cm^{-1}), we found that interactions between the hydroxyl end groups to the ether oxygen along the chain can affect the conformations quite differently between PEGs and PPGs. Due to this interaction, the difference in chain conformational distribution in PPGs has sufficiently different chain dynamics to affect the glass transition temperatures observed in DSC. These differences can be readily demonstrated by changing the end groups from hydroxy to methoxy. In contrast, PEG showed negligible end-group effects to the chain conformation distribution since no measurable differences were observed in the skeletal bending vibrations for the two types of end groups. Furthermore, based on our spectroscopic evidence, the interactions between end groups to the ether oxygen are critical in determining chain conformational distribution.

The interactions between the end groups seem to be less a perturbation in comparison to those along the chain. The methyl groups in PPGs appear to be extremely important in determining possible hydrogen-bond interactions and associated chain conformation, thus chain dynamics. Therefore, the increased chain flexibility by removing the hydroxy group in PPG may contribute to the increase of ionic conductivity of PPG-based polymeric electrolytes since the chain segmental mobility is known to be a predominant factor in determining ionic conductivity of the polymeric electrolyte system. Further studies will be conducted in this area.

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