Acoustic Relaxation of Liquid Poly(tetramethylene oxide) with Hydroxyl and Acyl Terminal Groups

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ABSTRACT: Isotherms of sound absorption and velocity vs. frequency were measured for poly(tetramethylene oxide)-2000 ended by CH₃ and OH groups. The measurements were performed at 5–2500 MHz and at different temperatures at 313–353 K. The results are presented and analysed using different formats to examine the frequency dependence of the attenuation $\alpha(f)/f^2 = f(f)$ and $\mu(f) = \alpha_{\text{exc}}(f)\lambda$ (where $\alpha(f)$ is sound attenuation at frequency f , α_{exc} is excess sound attenuation at frequency f , and λ is the sound wavelength) as well as frequency dependence of real (M') and imaginary (M'') parts of the mechanic modulus. Two dispersion regions are present on all sound absorption isotherms. Arrhenius curves of the relaxation time are fitted and analysed using Vogel–Tamann–Fulcher and Kohlrausch–Williams–Watts functions. Relaxation time in the first dispersion region, as well as relaxation strength, are less affected by the terminal groups of PTMO than in the second dispersion region. Alternation of the different end-capping groups has greater influence on the relaxation strength values of the second dispersion region characteristic of the local segmental motions of the polymers.

KEY WORDS Poly(tetramethylene oxide) / Ultrasonic Spectra / Relaxation Time /

The simplest aliphatic polyethers such as poly(methylene oxide) (PMO), poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and poly(tetramethylene oxide) (PTMO) are well known polymers and widely used for industry and fundamental scientific interest. However, PPO, because of its noncrystallizability and availability in a wide molecular weight range, is acceptable as a model object for close examination of relaxation properties of flexible chain polymers. Its relaxation characteristics, basically those of the corresponding low molecular weight OH-ended analogue, so-called poly(propylene glycol) (PPG), have been intensively studied using dielectric,^{1–6} optical,^{7–10} nuclear magnetic resonance (NMR),^{11–13} quasi-elastic neutron scattering,^{14, 15} and ultrasonic,^{16–21} techniques, as well as various methods for probing viscoelastic properties.^{22–24}

In contrast to PPO, PEO and PTMO are possible to crystallize and they can be closely investigated only in a temperature range above the melting point. Consequently, dynamics of such polyethers in their liquid/amorphous state is studied to a far lesser degree than that of PPG. There are a vast number of papers devoted to investigation of the relaxation features of OH-group end-capped low molecular weight PEO, poly(ethylene glycol) (PEG). The corresponding results are obtained using dielectric,^{25–27} NMR,²⁸ Brillouin

scattering,²⁹ and ultrasonic,^{30–32} techniques.

PPGs and PEGs are characterised for the most part by a presence of two room temperature dispersion regions, corresponding to the relaxation times of 10^{-8} and 10^{-10} s. Those of PEG and PPG are rather close to each other at the same temperatures.

It follows from the one paper³³ on relaxation behaviour of PTMO in a liquid state that room temperature quasielastic neutron spectra correspond to a relaxation time of 0.44×10^{-10} s. Some isolated experiments have been carried out to study relaxation characteristics of the amorphous regions of semi-crystalline PTMO using dielectrical,^{34, 35} and mechanical³⁶ relaxation techniques. It should be emphasised that PTMO is characterised by the smallest T_g , 178 K. Correspondingly, its “cooperativity plot” (*i.e.*, $\log \tau$ vs. T_g/T dependence),³⁷ has the smallest steep slope of the corresponding polyethers.

The molecular motions of the polyethers of the molecular weight about thousand g per mol may be grouped as:

–Relaxation processes related to Rouse normal mode motions (RM) with the relaxation time,³⁸ τ_{RM} , at room temperature of the order of 10^{-8} s.

–Local segmental motion (LSM) in the chain backbone (α -process) related to the dynamic glass transition, is always manifested in the relaxation spectra of

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the polyethers. LSM, as opposed to RM, is independent of molecular weight and its room temperature relaxation time is 10^{-9} – 10^{-10} s.

Concerning PTMO, in addition to a considerable importance in fundamental science for investigation relaxation processes in polymers the corresponding OH-group capped PTMO (PTMG) is extensively used in production of polymers such as segmented polyurethanes due to their unique physical properties,³⁹ ability to form water dispersions,⁴⁰ and ionene-like structures⁴¹, ability to develop a single-ion transport mechanism,^{42,43} and ease of materials to meet the specific use requirements.

A distinctive feature of PTMG as well as other OH-group-ended polyethers is possibility to develop hydrogen bonds between the OH groups as well as OH groups and ether groups of repeated units. It was supposed, by Heinlich *et al.*,⁴⁴ that molecular chains of PPG are connected at the ends by hydrogen bonds of the end OH groups forming so-called transient entanglements should strongly influence the relaxation of the polyether. However, in the case of PPG such a supposition was not confirmed by later investigations.⁶ To consider the effects of hydrogen bonding on the relaxation of PTMG two PTMO-based liquids investigated. The first is OH-group end-capped PTMO, so-called poly(tetramethylene glycol), PTMG. The second, acylated PTMG named PTMA, is -CH₃-group end-capped one. We normally think of acylated PTMO as a polymer not able to form, in contrast to PTMG, intermolecular O–H···O hydrogen bonds and its relaxation features are not affected by intermolecular transient entanglements.

EXPERIMENTAL

PTMG, of nominal molecular weight 2000, was purchased from DuPont and used as received. To prepare PTMA, acetylation of PTMG was carried out by adding 1.5 times excess acetic anhydride ((CH₃CO)₂O) (Aldrich) 293 K and allowing the reaction to proceed with backflow condenser for 2 h at 413 K. The product obtained was distilled under vacuum at 353 K and examined using IR spectroscopy.

Ultrasonic absorption measurements were performed at 313–353 K using pulse method at 5 MHz–2.5 GHz with an accuracy of 2···5%. The sound velocity was measured by a pulse-phase method with an accuracy of 0.1%. Instruments and procedures are described elsewhere.⁴⁵

Acoustic spectra obtained as involving two dispersion regions were resolved at each temperature, as first approximation, two Debye-like relaxation processes in

accordance with the formula

$$\alpha f^{-2} = \left(\frac{2\pi^2 c}{c_0^2} \right) \left[\frac{r_1 \tau_1}{1 + (\omega \tau_1)^2} + \frac{r_2 \tau_2}{1 + (\omega \tau_2)^2} \right] + B, \quad (1)$$

where $\omega = 2\pi f$; c is frequently dependent sound velocity; c_0 low frequency sound velocity ($\omega \tau_1 \ll 1$); r_i and τ_i relaxation strength and relaxation time for the i -th single relaxation region ($i = 1, 2$), respectively and B high frequency limiting αf^{-2} . To describe the frequency dependence of αf^{-2} the following empirical double relaxation equation was used

$$\alpha f^{-2} = \frac{A_1}{1 + (\omega \tau_1)^2} + \frac{A_2}{1 + (\omega \tau_2)^2} + B. \quad (2)$$

To determine $f_i = (2\pi \tau_i)^{-1}$ and A_i ($i = 1, 2$) and B eq 2 was solved using the iteration method.

Ultrasonic spectra are expressed frequently in the, so-called $\alpha_{\text{exc}} \lambda$ format, using the function μ that is excess sound absorption per wavelength,^{46–48}

$$\mu = \alpha_{\text{exc}} \lambda = \frac{(\alpha - B f^2) c}{f}, \quad (3)$$

where $\lambda = c/f$ is wavelength. In this case μ is evaluated as the sum of two relaxation processes by

$$\mu = \frac{2\mu_1 f f_1^{-1}}{1 + (f f_1^{-1})^2} + \frac{2\mu_2 f f_2^{-1}}{1 + (f f_2^{-1})^2} \quad (4)$$

μ_1 and μ_2 are maximum excess sound absorptions per wavelength at the respective relaxation frequencies f_1 and f_2 . Comparing eqs 2 and 4,

$$\mu_1 = \frac{A_1 f_1 c}{2} \quad (5)$$

and

$$\mu_2 = \frac{A_2 f_2 c}{2} \quad (6)$$

Using eqs 1, 2, 4, and 5, one can take r_1 and r_2 as

$$r_1 = \frac{2\mu_1}{\pi} = \frac{A_1 f_1 c}{\pi} \quad (7)$$

and

$$r_2 = \frac{2\mu_2}{\pi} = \frac{A_2 f_2 c}{\pi}. \quad (8)$$

Frequency dependence of the real, M' , and imaginary, M'' , part of the longitudinal modulus, $M^* = M' + iM''$ are conventionally calculated from frequency dependence of ultrasonic absorption, $\alpha(f)$, and velocity, $c(f)$, as,⁴⁹

$$M' = \rho c^2 \quad (9)$$

$$M'' = \frac{2\rho c^3 \alpha}{\omega} \quad (10)$$

Here ρ is density.

Taking into account eq 3 M'' is expressed as,

$$M'' = \frac{2\rho c^3}{\omega}(\alpha_{\text{exc}} + Bf^2) = \frac{2\rho c^3}{\omega}\alpha_{\text{exc}} + \frac{\rho c^3 f}{\pi}B$$

$$= M''_{\text{exc}} + \frac{\rho c^3 f}{\pi}B \quad (11)$$

M''_{exc} represents the α_{exc} -containing term and is more suitable for analysis in terms of width of relaxation time distribution than M'' .

In most amorphous polymers, loss modulus data in the vicinity of the peak when plotted against $\log \omega$, can be fit well by the Fourier transform of a Kohlrausch–Williams–Watts function (KWW).⁵⁰

$$\Phi(t) = \exp \left[-(t/\tau_i)^\beta \right] \quad (12)$$

where $0 < \beta \leq 1$ width of distribution of relaxation time, being unity for a single relaxation time. M'' must be found as Fourier transformation of the $\Phi(t)$ function,

$$M'' = M_r \int_0^\infty \cos(\omega t) \Phi(t) dt \quad (13)$$

to compare its profile with that calculated using acoustic spectroscopy data. Here $M_r = M_\infty - M_0$ is the difference between high- and low-frequency limiting M' .

RESULTS

Figures 1a and 1b show ultrasonic absorption isotherms of PTMA and PTMG samples, respectively, as function of frequency in the temperature range studied. At 10–40 MHz as well as 400–1500 MHz all α/f^2 vs. f dependency curves clearly display dispersion characteristics and adopt constant B at higher frequencies. Solid lines going through the measured values obey eq 4 and arrows in Figures 1a and 1b display positions of characteristic relaxation frequencies. In both samples, experimental α/f^2 are represented satisfactorily by the double relaxation equation.

Ultrasonic spectra of our samples are expressed in terms of μ (eqs 3 and 4) and exhibited in Figures 2a and 2b. The arrows display two relaxation regions on curves of frequency dependence of excess absorption per wavelength. The absorption effect characteristic of the high frequency region exceed that presented in the low frequency region by too large a margin. All μ against frequency curves are represented, as first approximation, by the sum of two Debye relaxations (solid lines in Figure 2) using eq 4. The relaxation frequency, f_1 and f_2 , the values A_1 , A_2 , and B parameters as well as μ_1 and μ_2 values are presented in Table I.

f_1 and f_2 , of PTMA and PTMG samples shift to high-frequency with increasing temperature and B decreases.

(a)

(b)

Figure 1. Frequency dependence of ultrasonic absorption of PTMA (a) and PTMG (b) at different temperatures. Arrows display positions of relaxation frequencies.

Replacement of CH_3 end groups with OH leads to decreasing f_1 and f_2 . In the case of f_2 , the decrease is higher than for f_1 . μ_1 and μ_2 decrease with increasing temperature. At 313 to 333 K, B of PTMG are lower than those of PTMA but after 343 K the reverse holds for B . In the temperature range considered μ_2 far exceeded (by the factor from 20 to 50) those of μ_1 and the higher is temperature, the greater is excess.

Sound velocity frequency dependence curves of PTMA and PTMG are presented in Figure 3. Marked sound velocity dispersion is characteristic of only the second relaxation frequency region.

The temperature dependency of the relaxation time of the first relaxation process, $\tau_1 = 1/(2\pi f_1)$, of PTMA and PTMG as well as that of the second relaxation are shown in Figure 4. τ_1 vs. $1/T$ dependency curves of both PTMA and PTMG appear closely allied and show that, at near-room temperature conditions, τ_1 are of the order of 10^{-8} s. The temperature dependency of τ_2 against $1/T$ of PTMA and PTMG, contrastingly, is different and corresponds to the different room temperature τ_2 of 1.78×10^{-10} and 3.16×10^{-10} s, respectively.

A sizeable increase in τ_2 is accounted for by the re-

(a)

(b)

Figure 2. Frequency dependence of excessive absorption of PTMA (a) and PTMG (b) at different temperatures. Arrows display positions of relaxation frequencies.

Table I. Temperature dependence of relaxation of CH₃ (PTMA) and OH-group (PTMG) end-capped low molecular weight PTMO

T, K	A_1	A_2	B	f_1	f_2	μ_1	μ_2
	$\times 10^{15} \text{Nps}^2 \text{ m}^{-1}$			MHz		$\times 10^4$	
PTMG-2000							
313	850	470	150	14	450	85	1523
323	560	370	110	17	510	66	1319
333	350	300	100	20	580	47	1193
343	230	250	90	23	655	35	1100
353	150	220	80	28	740	27	1052
PTMA-2000							
313	650	350	160	17	700	77	1711
323	420	260	130	20	850	58	1507
333	300	220	110	23.6	980	47	1444
343	190	193	90	28.9	1140	36	1429
353	120	166	75	35	1340	27	1413

placement of CH₃ end groups in the samples with OH. In contrast τ_1 increases a little in this case.

For polyethers the relaxation time *vs.* reciprocal temperature dependence obey, as a rule, the Vogel–Tammann–Fulcher (VTF) equation. Although the temperature range, in which the acoustic relaxation time

(a)

(b)

Figure 3. Frequency dependence of sound velocity of PTMA (a) and PTMG (b).

Figure 4. $1/T$ dependence of τ_1 and τ_2 of PTMA and PTMG. The solid curves are the approximations by VFT-equation.

data are obtained, is not wide enough to confirm VTF behaviour we used such an equation to fit the temperature dependence of the τ_1 and τ_2 .

$$\tau_i = \tau_{0i} \exp\left(\frac{B_i}{T - T_{0i}}\right) \quad (14)$$

Here τ_{0i} , B_i and T_{0i} are adjustable parameters and ($i = 1, 2$).

We believe VTF approximation is useful for comparing acoustic relaxation data obtained with the relaxation

Table II. Parameters for approximation of $1/T$ dependency of τ_1 and τ_2 were fitted by use of the VFT equation. I* and II* correspond to first and second relaxations, respectively

	PTMA-2000		PTMG-2000	
	I*	II*	I*	II*
$\log(\tau_0)/\text{sec.}$	-8.95	-10.33	-8.69	-9.7
B/K	300	250	270	180
T_0/K	140	145	140	145

Figure 5. Temperature dependence of r_1 (a) and r_2 (b) of PTMA and PTMG.

data temperature dependence on PTMO obtained by other authors using different experimental techniques. VTF approximating curves are shown in Figure 4 by solid lines and τ_{0i} , B_i and T_{0i} are listed in Table II. For the first relaxation the eq 14 parameters are altered but little after replacing CH_3 end group with OH. But τ_{02} and B_2 decreased markedly.

Figure 5a shows r_1 against temperature curves for PTMA and PTMG. r_2 vs. T curves are drawn in Figure 5b. Relaxation strength of the first relaxation process, r_1 , of PTMA and PTMG is a monotonically decreasing function of temperature. The corresponding relaxation strengths should follow,

$$r_1 \sim T^{-\delta} \quad (15)$$

and exponents, δ , obtained are of the order of 9 for

Figure 6. Frequency dependence of real modulus, M' , of PTMA (a) and PTMG (b) at temperatures studied.

PTMA and PTMG.

The temperature behaviour of r_2 is different from that of r_1 . First, for PTMA and PTMG, bi-logarithmic plots of the r_2 data, in distinction to those of r_1 , are non-linear in T . Second, the corresponding temperature dependencies of r_2 are far less steep in comparison with those of r_1 . Thirdly, bi-logarithmic r_2 vs. T plots of PTMA are far less steep than for PTMG.

In general, the temperature behaviour of μ_1 and μ_2 should be similar that of r_1 and r_2 . Comparing r_1 and r_2 as well as the μ_1 and μ_2 exhibit very strong distinctions. At all temperatures, r_2 (μ_2) are far above the corresponding r_1 (μ_1).

Frequency dependence of M' for PTMA and PTMG at the temperatures indicated are shown in Figure 6. The only jump, in the vicinity of f_2 , occurs in a family of M' vs. frequency isotherms. This is in line with the fact that in the case of PTMA as well as in PTMG the sole non-negligible velocity dispersion takes place.

Sets of $M''(f)$ for PTMA and PTMG are plotted in Figure 7. The solid lines represent M'' calculated according to the eq 10 from the approximating α/f^2 curves of Figures 1 and 2. All of the corresponding

(a)

(b)

Figure 7. Frequency dependence of loss modulus, M'' , of PTMA (a) and PTMG (b) at temperature range studied.

isotherms are characterised by two weakly pronounced maxima at frequency close enough to the corresponding f_1 and f_2 in Table I.

To compare the frequency behaviour of M'' curves at different temperatures we reduced all to obtain a master plot to the M'' data at 313 K, using the corresponding f_2 for determination of a horizontal displacement $\log\left(\frac{f_2^T}{f_2^{313}}\right)$ (f_2^{313} is f_2 at $T = 313$ K and f_2^T that at other temperatures used). The reduced M'' curves for PTMA and PTMG are presented in Figure 8. M'' data sets taken at various temperatures and reduced to the same temperature do not fall on a single composite curve for both polymers. Particularly striking is the considerable variation from one reduced curve to another at low frequency portions.

Relaxation characteristics can be investigated from plots of the imaginary modulus M''_{exc} . Second M''_{exc} spectrum maxima of all the isotherms were normalized relative to each other to represent of them as $M''_{\text{exc}}/M''_{\text{exc,max}}$ vs. $\log(f/f_2)$. In this case M''_{exc} is the frequency dependent M'' value and $M''_{\text{exc,max}}$ is the corresponding maximum of M''_{exc} . The eq 13 was used to cal-

(a)

(b)

Figure 8. Loss modulus, M'' , measurements on PTMA (a) and PTMG (b), reduced from different temperatures used to 313 K with shift factors calculated from a position of the high-frequency maximum.

culate the profile of the τ_2 -based maximum. The corresponding normalised M''_{exc} isotherm data for the second dispersion region fall on a single composite curve presented in Figures 9 (maximum the M''_{exc} vs. f curves of PTMA (open symbols) and PTMG (solid symbols)). Model M''_{exc} spectra that were taken at different β , such as 0.7, 0.9, and 1.0, are presented in Figure 9. β for PTMA and PTMG are rather close to unity.

The glass transition temperature, T_g , of PTMA and PTMG are calculated from VTF equation presented in Table II. We defined T_g as the temperature at which the segmental relaxation time equals 1 s. The corresponding T_g were 171 and 165 K for PTMA and PTMG, respectively, close enough to that of semi-crystalline PTMO³⁷ (178 K). Cooperativity plots (τ_2 vs. T_g/T curves³⁷) were calculated for a liquid state of PTMA and PTMG. These plots in comparison with the cooperativity plot of semi-crystalline PTMO, taken from,³⁷ are presented in Figure 10. Cooperativity plots obtained lie below plots of semi-crystalline PTMO and are steeper.

Figure 9. Normalised second maxima of the M''_{exc} spectra of the PTMA (open symbols) and PTMG (solid symbols) samples.

Figure 10. Segmental relaxation time as a function of normalized temperature, T_g , for liquid PTMA ($T_g = 171$ K) and PTMG ($T_g = 165$ K) obtained by ultrasonic relaxation spectroscopy (this work) in comparison with the corresponding dependence for semi-crystalline PTMO obtained by dielectric relaxation spectroscopy, 37, and neutron spectroscopy, 35.

DISCUSSION

Types of Relaxation

All the spectra shown in Figure 1 have similarities to those of the low molecular weight polyethers considered above. In Table I, characteristic frequencies of PTMG in the temperature region from 313 K to 333 K are 14–20 MHz and 450–580 MHz for the first and second dispersion region, respectively. It is interesting to compare the relaxation times observed with the corresponding data presented by the only paper⁵ on high frequency dielectrics of PPG of molecular weight 2000 at near-room temperatures.

If we compare PTMG relaxation times calculated using the characteristic frequency data presented in Table I with those presented by paper⁵ the low frequency region and at near-room temperatures the PPG data are about 10^{-8} and 10^{-10} s for low frequency and high fre-

quency region, respectively. Closed relaxation times for both frequency regions are characteristic of PTMG and PTMA. Particular, what about the low frequency region, we have seen that the difference between them is not larger than 10–15%. The corresponding difference for high frequency region is in the range 30–50%. Taking into account that PPG is partly similar but different from PTMG, dielectric and acoustic relaxation times of the first relaxation of PPG2000 and PTMG2000, respectively, are very close to say that the first relaxation process observed in the acoustic spectra of PTMG as well as PTMA are of RM type one. High frequency relaxation can be considered as the LSM, or structural relaxation, process.

Comparison of τ_1 and τ_2 against temperature and presented in Figures 4 showing of end group influence on the LSM region is more than on the RM relaxation region of the acoustic spectra of the PTMO-based low molecular weight polymers. The temperature behaviour of relaxation strength in the first relaxation region, r_1 , in Figures 5a and 5b for PTMA and PTMG is the same and it is in line with that of most polymers. Consequently, whether or not molecular chain ends are H-bond connected, the RM relaxation related to equilibrium conformation transitions are practically the same. Relaxation times of structural relaxation as well as relaxation strength are thus more sensitive to the replacement of OH end groups with CH_3 than those of large scale motion unaffected by such a replacement. This was completely confirmed by normal mode relaxation in OH group ended PPG as well as acylated one.⁶ The latter evidences that the effect of hydrogen bonding between the OH groups on the normal mode relaxation time is negligibly small.

A few intermolecular H-bonds radically slow down LSM relaxation (compare f_2 of PTMA and PTMG in Table I). In LSM relaxation region, decrease of relaxation strength is more pronounced for H-bond connected molecular chain (OH ended chain) in comparison with that of the free end one (CH_3 ended chain).

The steep rise of M' in PTMA and PTMG M' vs. f curves (Figure 6) that occurs only in the vicinity of f_2 at all the temperatures is certain to be of dynamic glass transition (α -relaxation) origin. This is good verification of the nature of the second relaxation process in the samples studied as of one related to the LSM mechanism.

Thermoreological Simplicity/Complexity

Temperature change leads to the change of the characteristic frequency in the wide frequency interval. If the time-temperature superposition can be applied to the processes under consideration, it should be possi-

ble to convert the temperature domain experiment into the frequency domain one. The ultrasonic absorption data at any T have to be superimposed exactly on the corresponding points taken at reference T , T_{ref} , by a horizontal displacement $\log \frac{f_2(T)}{f_2(T_{\text{ref}})}$.

Sets of M'' vs. f isotherms in Figure 7 provide the possibility of analysis of first and second relaxations in the context of thermoreological simplicity/complexity alternative.³⁷ In Figure 8, reduction to a reference temperature based on the position of the M'' second relaxation maximum leads to splitting of the curves reduced in the vicinity of the first relaxation maximum. The temperature behaviour of the M'' vs. f curves in the frequency range on first relaxation maximum and second one is different. Therefore, the thermoreological simplicity hypotheses is not applicable for the polymeric liquids studied.

For polyethers, only one absorption peak corresponding to dynamic glass transition (LSM, *i.e.*, α -relaxation), is usually observed in the temperature dependence of M'' at a constant frequency obtained by ultrasonical technique^{51, 52} and no such absorption related to RM relaxation is present on the corresponding curves. This is in contrast with the present investigation on PTMO-based short chain polymers carried out showing two absorption maxima at 5–2500 MHz. Obviously, ultrasonic temperature domain investigation of polyethers is useful to give a quick glimpse of all the temperature relaxation transition. However, the results obtained can lead to a loss of some peculiarities of the relaxation spectra and, what is more, cannot be used to a rigorous analysis of the data in the frame of the molecular dynamic models used.

The Relaxation Spectra Parameters

Most if not all dynamic processes in polymers should have a distribution of relaxation times. Not far above T_g and at long relaxation times a rather broad distribution of relaxation times was observed.^{53–55} Such “non-exponential decay” is explained by the coupling model.³⁷

When the observed relaxations are due to single relaxation (Debye-like relaxations), the ultrasonic absorption coefficient can be represented by eqs 1 and 2. This is the limit $\beta = 1$ of eq 6 that describes the Debye case with a single relaxation time and after fitting the observed data by eq 2 we find parameters of a relaxation process in such an approximation.

From dielectric measurements, for polyethers such as PPG, the normal mode relaxation at near-room temperatures is practically Debye-like and the shape parameters for such processes were assumed to be near unity.⁵

In contrast to normal mode relaxation at the room temperature, LSM is usually characterised by wider distribution of relaxation time. For some liquids, such as ionic glass forming one, the broad distribution of relaxation times, as the material moves away from T_g , sharpens up to become a single relaxation time in the high frequency region at elevated temperatures.⁵⁶ However, for short chain polyethers there is no general agreement regarding the temperature change of the relaxation time distribution. At room temperature Brillouin spectra of PPG, related to hindered LSM relaxation can be fitted to theoretical values using single relaxation time behaviour.⁵⁷ The results of another Brillouin experiment as well as the near-room temperature dielectric measurements⁵ show that single relaxation time theory cannot explain LSM α -relaxation behaviour of the polymer.¹⁰ For liquid PTMG, in accordance with Allen *et al.* using quasi-elastic neutron investigation,³⁵ β was far smaller than unity at temperatures above the room temperature. Thus, for the polymers such as short chain polyethers there is no general agreement regarding the near-room temperature relaxation time distribution.

Modelling normalised M''_{exc} vs. f curves presented in Figure 9 show, at more than 120 K above the T_g , for both PTMA and PTMG no broadening relaxation time of LSM relaxation. So in the near-room temperature range the LSM motions of these polyethers are characterised by a rather single relaxation time and the coupling parameter, $n = 1 - \beta$, tends to zero.

It was interesting to compare plots of the LSM relaxation of the liquid samples with the corresponding data obtained for liquid PTMO involved in the neutron spectroscopy investigation³⁵ and cooperativity plot of semicrystalline PTMO.³⁷ Figure 10 shows that plots of PTMA and PTMG to lie just above the neutron spectroscopy data and well below plot of semi-crystalline PTMO.

CONCLUSION

Two relaxations were found from acoustical spectrum of the PTMO-based oligomer liquids with CH_3 and OH end groups at 5–2500 MHz and 313–353 K. The higher relaxation times, τ_1 , as well as the lower relaxation times, τ_2 , are close to the relaxation time characteristic, at room temperature, of local segmental motion (so-called dynamic glass transition). The latter relaxation region precisely corresponds to only one marked sound velocity dispersion. Relaxation time and strength at different temperatures are sensitive to replacement of OH end groups with the CH_3 while large scale motion is unaffected by such replacement.

OH end groups and H-bonding networks slow down local segmental motion relaxation and increase relaxation strength.

Using imaginary modulus against frequency curves, breakdown of thermoreological simplicity in the frequency range was found to occur and RM and LSM relaxations are Debye-like.

Temperatures studied the τ_i vs. inverse temperature dependency may be approximated by VTF equation. The corresponding τ_1 vs. $1/T$ curves for CH₃ and OH ended samples coincide but τ_2 vs. $1/T$ ones are very different. Plots drawn for the high frequency absorption region show that curves approximating τ_2 vs. T_g/T data are far below the corresponding curves obtained by K. L. Ngai and C. M. Roland for semi-crystalline PTMO and close enough to τ_2 vs. T_g/T data calculated using the neutron spectroscopy data obtained by Allen *et al.* for liquid PTMO.

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