Influence of hydrogen bonds on the properties of low molecular weight polyoxypropylene, as studied by nuclear magnetic resonance and thermodynamic measurements: further indication for a transient entanglement

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Nuclear magnetic resonance (n.m.r.), differential scanning calorimetry (d.s.c.) and thermodynamic measurements were performed in polypropylene glycol (PPG) melts with molecular weights ranging from 520 to 3200 g mol^{-1}. They are compared with recent ultrasonic experiments showing local modes, normal modes, and a characteristic low frequency relaxation in samples with $M_w > 1300$ g mol^{-1}. This additional relaxation process for higher molecular mass material was also detected by n.m.r. measurements. As an explanation for this process, a special entanglement between transient intermolecular structures formed by hydrogen bonds and having effective molecular weights above the critical values is discussed.

(Keywords: transient entanglement; hydrogen bond; n.m.r.; thermodynamic measurements; polyoxypropylene)

INTRODUCTION

In the measurements of viscoelastic properties[1,2] and in ultrasonic measurements[3-5], the existence of an additional low frequency relaxation (E) for higher molecular mass samples of polypropylene glycol (PPG) was found. The nature of this process has been discussed in several contradictory ways. Two ways of explaining this process have been proposed in the literature: by normal mode motions[1,2] or by entanglements[3]. In a previous paper[4], we assumed that this process is connected with a special entanglement between transient intermolecular structures formed by hydrogen bonds and having effective molecular weights above the critical values. A more detailed theoretical model for this hypothesis will be given elsewhere[6].

In dielectric relaxation measurements of polypropylene oxide systems[7-11], three different relaxation processes have been detected. The β process was explained by local motions in the chain backbone[9-11]. At temperatures above 250 K this process coincides with the α process, which can be related to the dynamic glass transition[7-11]. The so called α' process, located below the α process in the relaxation map, has been supposed to be related to the normal mode contribution[7,9-11]. Contrary to the additional low frequency process in ultrasonic[4,5] and viscoelastic[1] measurements, the α' process in the dielectric relaxation does not disappear by conversion of the hydroxyl end groups[7], and its intensity increases relative to the α process if a solvent is added or the molecular mass is decreased[10].

This paper shows that additional n.m.r. relaxation, d.s.c., and thermodynamic measurements in PPG melts with molecular weights in the range 520–3200 g mol^{-1} give further evidence for our transient entanglement hypothesis in PPG melts with molecular mass below the critical value ($M_c \approx 7000 > M_w > M'_w \approx 1300$).

EXPERIMENTAL

Oligomer preparation

The PPGs used are the same as in references 4 and 5. They were prepared by potassium hydroxide catalysed polymerization. The polymers were dried *in vacuo*. The samples were expected to be linear chains with a low polydispersity ($\bar{M}_w/\bar{M}_n < 1.2$), having only head-to-tail structures, and terminated by hydroxyl groups[12]. One of the samples ($M_n = 2880$) was treated with trimethylchlorosilane in order to convert the hydroxyl end groups to trimethyl silyl groups. ^{13}C n.m.r. analysis shows that, after conversion, the number of hydroxyl groups is reduced to less than 5%[13]. Therefore, only a low number of hydrogen bonds is expected to occur in this sample (PPOS). The molecular weights of the samples are listed in *Table 1*.

N.m.r. measurements

The proton spin–lattice relaxation times T_1 at $f = 22$ and 88 MHZ and $T_{1\rho}$ (rotating frame) were measured as a function of temperature by means of a slightly modified Bruker spectrometer (SXP 4/100).

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Table 1 Characteristic data of the samples

Sample	M_n	Terminal groups
PPG 10	980	hydroxyl (diol)
PPG 30	2660	hydroxyl (diol)
PPOS 30	2740	trimethyl silyl

Vapour pressure measurements

The solvent partial vapour pressures, P_A, of the polymer solutions were measured using an isopiestic vapour–sorption method[14,15]. Toluene and n-decane were used as solvents. The experimental data are reduced to the $\chi = \bar{\mu}_A^E/RT\phi_B^2$ function using the reduced segment molar excess chemical potential $\bar{\mu}_A^E$ of the solvent A[16]:

$$\chi = (\ln(P_A/P_{A*}) - \ln(1-\phi_B) - (1-1/r_B)\phi_B - k_A)/\phi_B^2$$

$$k_A = (V_{A*}^L - B_{AA})(P_A - P_{A*})/RT$$

where R is the molar gas constant, T is the temperature, P_{A*} is the pure solvent vapour pressure, B_{AA} is the correspondent second virial coefficient, V_{A*}^L and V_{B*}^L are the liquid molar volumes of the pure solvent and polymer, respectively, ϕ_B is the volume fraction of the polymer, and $r_B = V_{B*}^L/V_{A*}^L$ is the number of polymer segments.

For n-decane at 343 K we used values of $P_{A*} = 2600$ kPa, $B_{AA} = -2950$ cm^3 mol^{-1} and $V_{A*} = 2039$ cm^{-1} mol^{-1}.

D.s.c. measurements

The glass temperatures, T_g, were determined in a DSC-1B from Perkin Elmer at a scan rate of +8 K min^{-1}. The T_g values at 199, 201 and 202 K (±2 K), obtained for PPG with molecular weights of 520, 980, and 2660, respectively, showed that the main relaxation is hardly influenced by the chain length in this region. No crystallization effects could be detected.

RESULTS AND DISCUSSION

Molecular weight dependence

The ultrasonic absorption data given in references 4 and 5 showed that the high frequency range of the spectra (above a few megahertz for $T = 308$ K) is relatively independent of molecular mass. In this region the ultrasonic absorption and the dynamic shear viscosity spectra can be described by a frequency dependence proportional to f^{-n} with $n \approx 0.2$–0.3. Attempts have been made to describe this frequency range in terms of the subchain concept[4]. The low exponent of the frequency dependence of the normal mode spectra, in comparison to the Rouse exponent, was explained by a modification of the specific segmental interactions in the melt instead of the solvent environment[4,17]. Similar exponents were obtained for the normal mode region of low molecular mass polybutadiene melts[18]. The local motions are indicated by ultrasonic measurements[4] at about 600 MHz. They are in agreement with the α process in dielectric relaxation[7–12].

Samples with higher molecular weights ($M_w > M'_w$, see below) change their frequency dependence in ultrasonic spectra in the low megahertz region. This E relaxation could also be observed in ultrasonic measurements for star-shaped molecules ($M_n = 2050$)[5]. The same type of frequency dependence was obtained for both effective (proportional to the ultrasonic absorption α/f^2; $\eta_{eff} = \eta'_s + (3/4)\eta'_v$) and dynamic shear viscosities (η'_s) of two PPG samples ($\eta_{eff}/\eta'_s \approx 2$)[5]. The additional relaxation process is connected with both dynamic shear (η'_s) and dynamic volume (η'_v) viscosity. Similar behaviour could be detected in entangled polybutadiene melts[18].

The molecular weight dependence of the static shear viscosity[4,5] changed its exponents from 0.6 to 1.4 at an (interpolated) characteristic molecular weight of $M'_w \approx 1300$.

The results of the n.m.r. relaxation time T_1 and $T_{1\rho}$ measurements for PPG 10 ($M_w < M'_w$) and PPG 30 ($M_w > M'_w$) are given in *Figures 1* and *2*. The double T_1 minimum and the $T_{1\rho}$ minimum are due to the main transition (dynamic glass transition). It has been suggested[19] that the splitting of the T_1 minimum is due to the different mobilities of protons in the chain backbone and the side group protons.

The additional E relaxation process in PPG 30 ($M_w > M'_w$) is indicated by a shoulder in the high temperature flank of the curves which is absent in the PPG 10 ($M_w < M'_w$) sample. Its location in an Arrhenius diagram (see *Figure 3*) shows a connection with the change in the ultrasonic relaxations in the megahertz region.

As briefly mentioned in reference 4, three possibilities can be discussed for explaining the additional relaxation process for molecular weights above M'_w. To avoid misunderstanding we shall discuss the situation again in a more precise way:

Subchain motions[1,2]. Although this possibility cannot be excluded with certainty, there is some evidence against

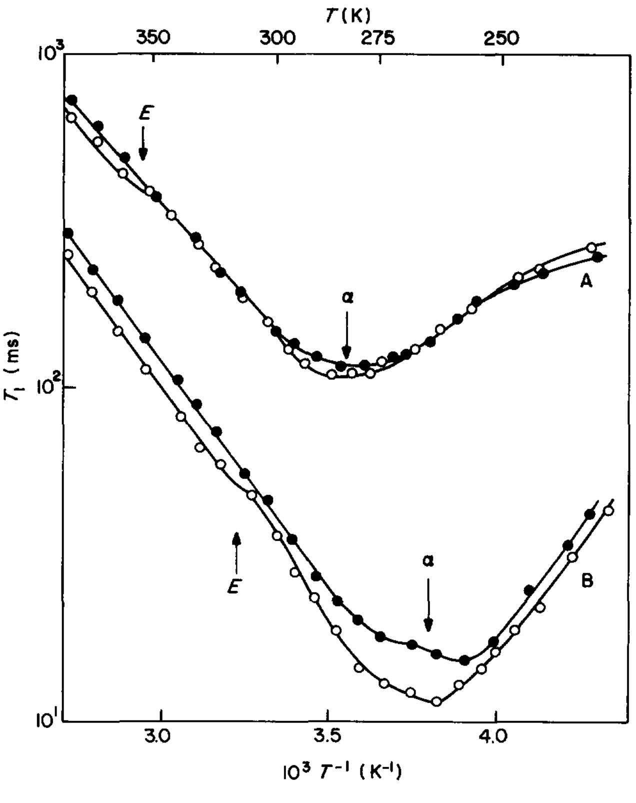

Figure 1 Temperature dependence of the n.m.r. relaxation times (T_1) at two different frequencies (A, 88 MHz; B, 22 MHz) in PPG: ○, $\bar{M}_n = 980$; ●, $\bar{M}_n = 2660$. For clarity, the ordinate for the 22 MHz data is displaced by a factor of 0.5. The marks E (additional relaxation) and α correspond to the annotations in *Figure 6*

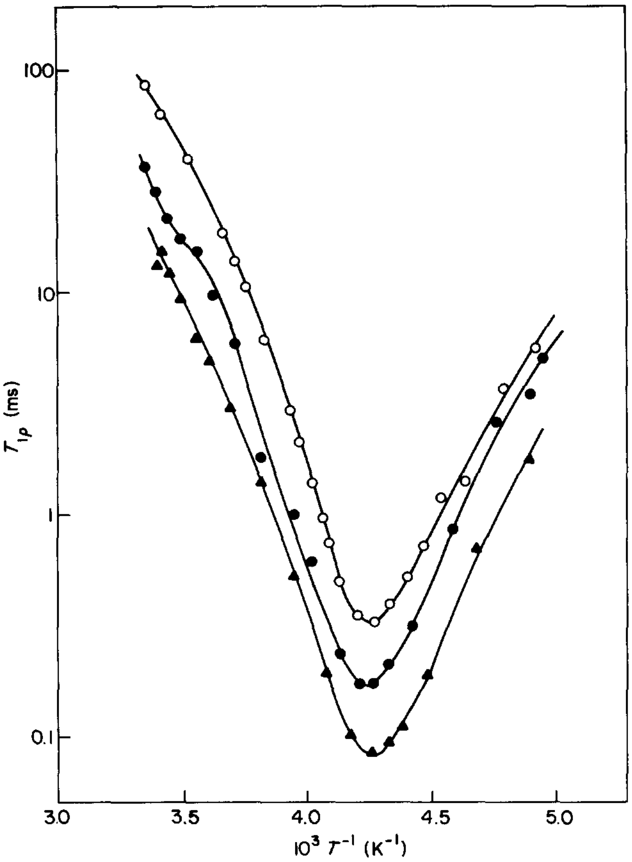

Figure 2 Temperature dependence of the n.m.r. relaxation time ($T_{1\rho}$). ○, $\bar{M}_n = 980$ (PPG 10); ●, $\bar{M}_n = 2660$ (PPG 30); ▲, $\bar{M}_n = 2740$ (PPOS 30, trimethyl silyl). The ordinates are successively displaced by a factor of 0.5 with respect to the sample PPG 10

the assumption that the onset of normal modes is responsible for the additional low frequency relaxation. Using a solvent it could be demonstrated[4,5] that the frequency of the additional relaxation is quite independent of the polymer concentration for $\phi > 0.6$. But the relaxation could not be detected for lower concentrations $\phi < 0.6$. Furthermore, the additional process in acoustic and n.m.r. measurements is connected with the existence of hydroxyl end groups (see below). It is difficult to describe this behaviour in terms of subchain motions. On the other hand, in all acoustic measurements[3-5] one can obtain a broad relaxation time spectrum in the frequency range 5–100 MHz which can be explained by subchain motions (normal modes modified by segmental environment in the melt, as mentioned in the introduction). Otherwise there would be a gap of more than one frequency decade between the local modes (expected near 600 MHz[4,7-9]) and the normal modes. It is possible to explain the differences mentioned between the α' process in dielectric measurements and our additional process in ultrasonic and viscoelastic measurements. The entanglement (also the special entanglement) is normally located at the low frequency limit of the normal mode spectra. As there is a different sensitivity (activity) of mechanical and dielectric measurements for different modes, one can assume that ultrasonic and viscoelastic measurements can detect our special entanglement, whereas the dielectric experiment is only sensitive for higher normal modes. Therefore we assume that the α' process and our additional relaxation for $M_w > M'_w$ are nearly parallel curves in the relaxation map.

Hydrogen bond kinetics. As the additional relaxation is observed for higher ($M_w > M'_w$) molecular weights where the concentration of hydroxyl groups is low[20], the hydrogen bond kinetics cannot be directly[6] responsible for the effect. However, these processes can occur outside the frequency and temperature region considered here.

Entanglement effects[3]. Since the molecular weights of all samples are below the critical values, $M_w < M_c \approx 7000^{21}$, a classical entanglement can also be excluded. However, all the other experimental phenomena do not rule out the possibility of entanglements. Therefore we assume our transient entanglement due to hydrogen bonds.

'Chemical deassociation' and solvent influence

In order to test our hypothesis of entanglement effects in transient structures ($M_{eff} > M_c$) formed by hydrogen bonds, we attempted to destroy them by converting hydroxyl groups ('chemical deassociation') or by adding a non-polar solvent.

A comparison between PPG 30 (with hydroxyl end groups) and the converted PPOS 30 (with no or only a small number of hydroxyl end groups) is made for the n.m.r. relaxation time T_1 (*Figure 4*), $T_{1\rho}$ (*Figure 2*), and the effective viscosity η_{eff} (*Figure 6* of ref. 4). As expected, the additional relaxation cannot be detected using the mechanical and n.m.r. methods in the converted samples.

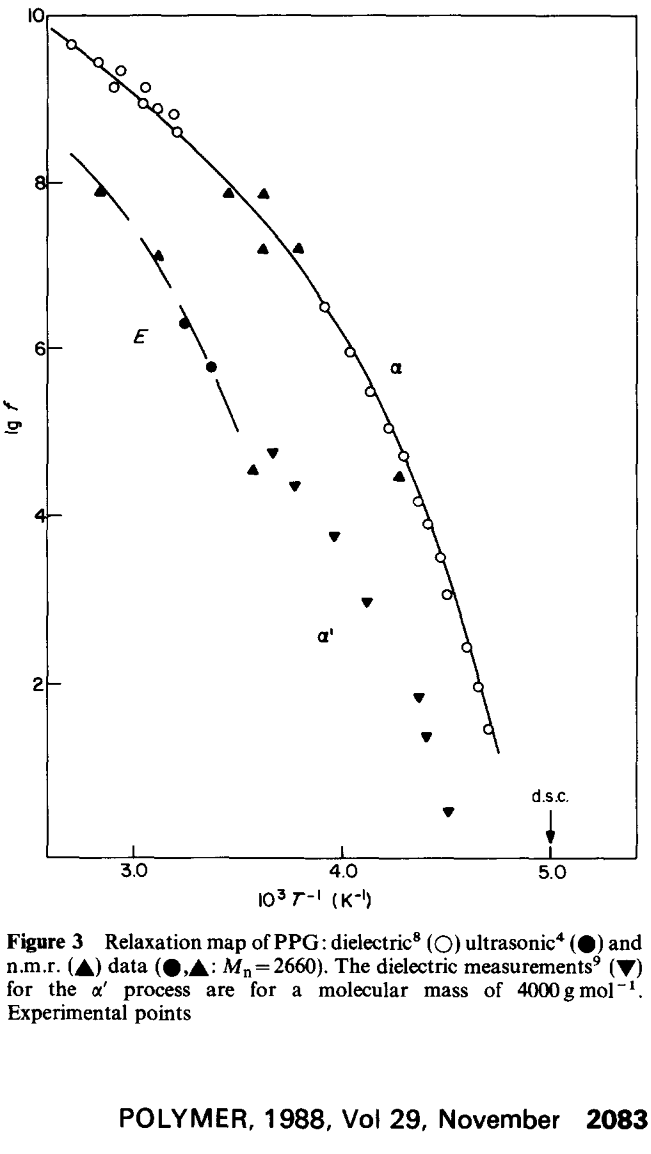

Figure 3 Relaxation map of PPG: dielectric[8] (○) ultrasonic[4] (●) and n.m.r. (▲) data (●,▲: $M_n = 2660$). The dielectric measurements[9] (▼) for the α' process are for a molecular mass of 4000 g mol^{-1}. Experimental points

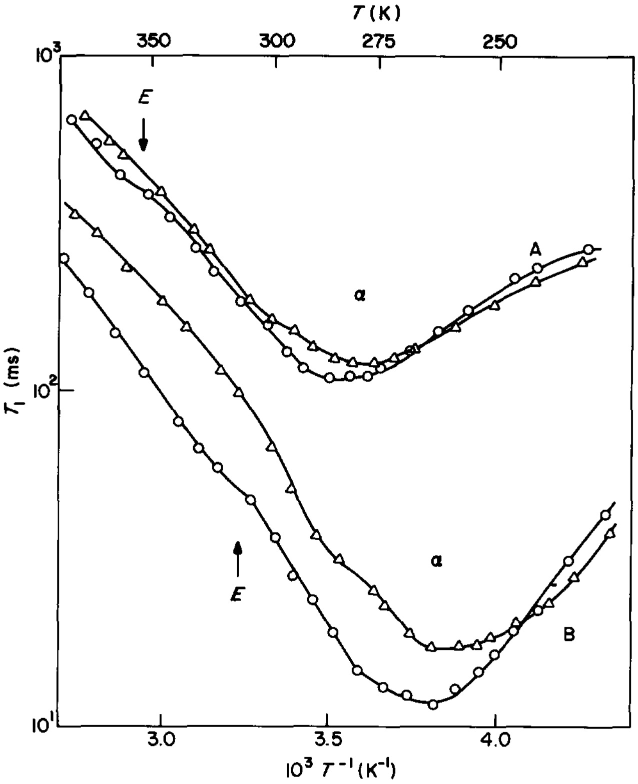

Figure 4 Temperature dependence of the n.m.r. spin-lattice relaxation times at (A) 88 and (B) 22 MHz in polypropylene glycol (PPG 30, ○) and in the sample with converted hydroxyl groups (PPOS 30, △). For clarity, the ordinate for the 22 MHz data is displaced by a factor of 0.5

Furthermore, it is difficult to understand this fact in terms of subchain motions because the main chain is not altered by the conversion of the terminal groups. This result contradicts the results of a similar dielectric experiment (conversion of hydroxyl end groups to methoxyl groups) by Bauer and Stockmayer[7], where the dispersion of the α' process did not disappear. This supports our assumption of two different processes (additional ultrasonic or n.m.r. relaxation and the α' relaxation), differing in molecular nature and the resulting activity.

Using n-decane as a solvent[4], the additional relaxation could be detected in ultrasonic absorption only for the higher polymer volume fractions $\phi = 1$ and 0.8. This is in accordance with our assumption that the solvent leads to a 'depolymerization' of the associates when the effective molecular mass $M_{\text{eff}} = M_{\text{eff}}(\phi)$ decreases below M_c, whereas the subchain modes are expected to be less influenced by the solvent.

Our view is also supported by the behaviour of the χ parameter of PPG 30 and PPOS 30 in n-decane (*Figure 5*). The marked difference between the two curves above $\phi > 0.7$ can be explained by the absence of associative structures in the converted PPOS 30 sample containing no hydroxyl groups. At $\phi \approx 0.7$ the χ values of the two solutions are similar which means that there are only little effects here due to the hydrogen bonds.

Relaxation map

A further indication for our transient entanglement hypothesis can be obtained from the localization of the additional E relaxation in an Arrhenius diagram (*Figure 3*). The glass transition (α) of PPG with comparable molecular weight is consistently documented by dielectric[7-9] and our n.m.r. relaxation, ultrasonic[4] and d.s.c. data.

The additional relaxation (E) for $M_w > M'_w$ is also consistently documented by the ultrasonic and n.m.r. data. Its relative localization corresponds to a terminal zone (flow transition) for macromolecules having molecular weights of several $10^4\,\text{mol}^{-1}$, i.e. $M_{\text{eff}} > M_c$.

It must be noted here that the dielectric data for the α' process plotted in the relaxation map, are for a molar mass of $4000\,\text{g mol}^{-1}$ (ref. 9). Because of the molar mass dependence of normal modes, which are assumed to be responsible for the α' process, the α' process for a comparable molar mass ($2600\,\text{g mol}^{-1}$) should be shifted to higher frequencies by a factor of about two. This location would support our assumptions about the different molecular nature and activity of the additional relaxation and the α' process.

Discussion of a model for our hypothesis

We think that our model can give a consistent description of the various experiments. Transient network entanglement effects are already known from investigations in inorganic glass. A plateau region in shear experiments with small stresses was reported by Bartenev[22]. The inorganic glass was considered to be a

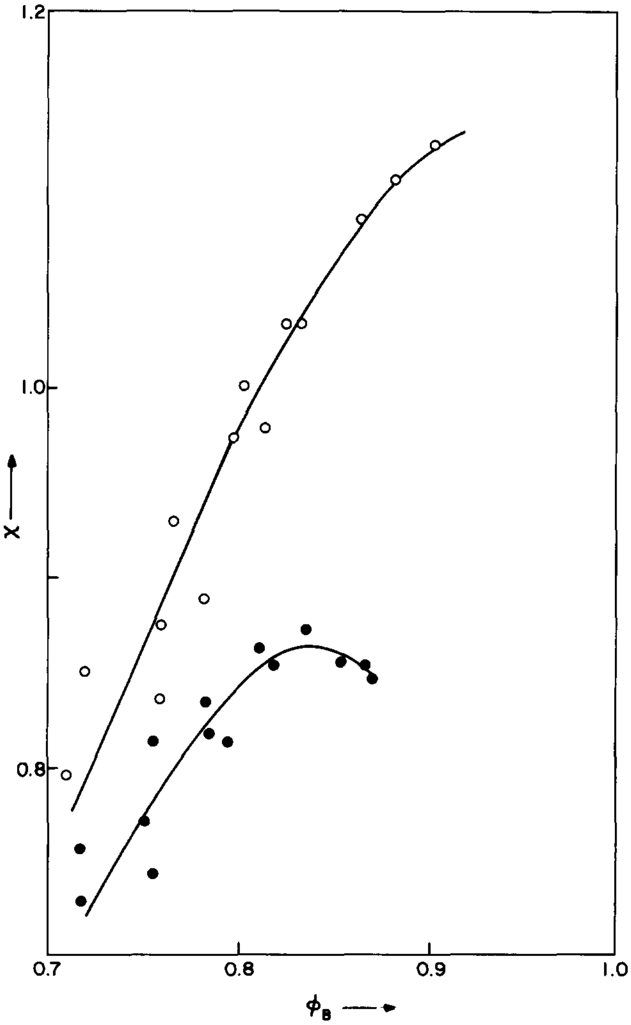

Figure 5 χ function in the systems n-decane/PPG 30 (●) and n-decane/PPOS 30 (○) at 343 K

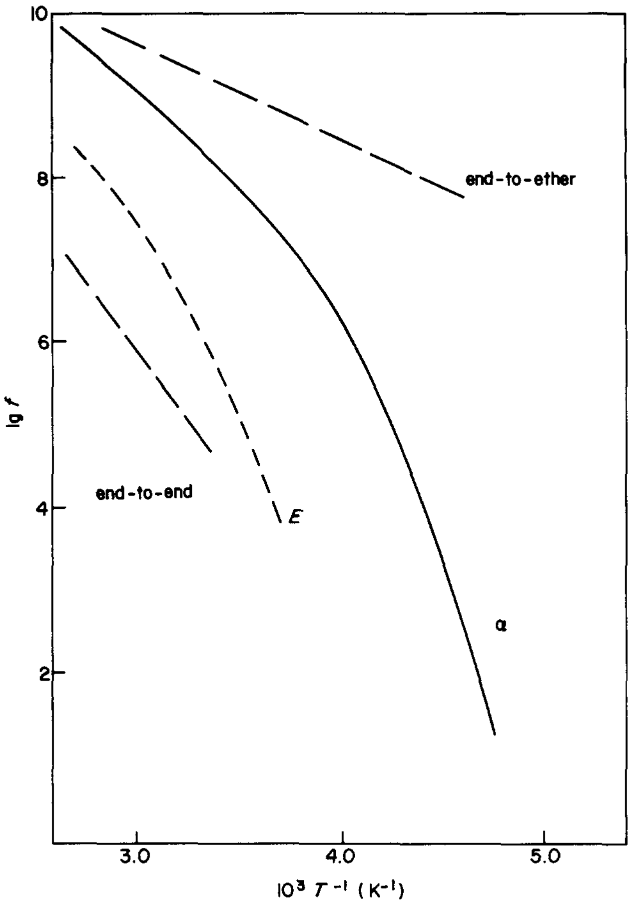

Figure 6 Suggested relaxation map with the dynamic glass transition (α), the transient entanglement (*E*) and the presumed relaxations of hydrogen bonds

network polymer with low molecular weight of the network chains. Similar effects were found by Coenen[23].

If we assume transient intermolecular structures formed by hydrogen bonds to be responsible for our entanglement effect, it is necessary to make some assumptions about the nature and the kinetics of the different types of hydrogen bonds.

The lifetime of these supermolecules must be long enough to form entanglements (i.e. for reptation). Therefore it is necessary to have access to information about hydrogen bond dynamics. No direct reference for hydrogen bond kinetics in PPG were found in the literature. However, the existence of different types of hydrogen bonds is well established from i.r. investigations of PPG and PEG systems[20,24]. The terminal hydroxyl groups of the PPG chain are known to be able to form two types of hydrogen bonds: end-to-end and end-to-ether oxygen. Both can form intra- and intermolecular structures (intramolecular rings, branched structures, longer chain structures). For low molecular weights, many such structures should exist because of the high concentration of hydroxyl end groups. For increasing molecular weight the possibility of intramolecular hydrogen bonds decreases, because it is rather improbable that the hydroxyl end groups attack the ether atoms or the second terminal group of their own chain, if the coiled interpenetrating chains are long enough. In this case, from a statistical point of view, one would expect that the configurational probability for intramolecular hydrogen bonds between the terminal hydroxyl groups and the ether atoms is much higher than for the end-to-end type. The fact that i.r. experiments[20] in PPG melts of higher molecular mass can actually detect different molecular mass dependences for the two types, although the end-to-end type is not very probable, leads to the conclusion that the end-to-end type hydrogen bond must be energetically favoured, i.e. must be much stronger than the end-to-ether one. Lirova *et al.*[20] assumed for the end-to-end type hydrogen bond a OH ... OH ... O multimer. But the special nature of this bond (cf. ref. 24) is not of any great importance for our model.

The assumption of different strengths for the two types of intermolecular hydrogen bonds is necessary for our model. End-to-ether hydrogen bonds, which would form a polymer network, are assumed to be weak.

Therefore, we can assume that the curve of the hydrogen bond kinetics (OH ... O) is located above the α process of PPG in an Arrhenius plot (*Figure 6*). This means that the lifetime of these branched structures is too short to influence our transient entanglement and the dynamic glass transition.

The end-to-end hydrogen bonds are assumed to form relatively strong intermolecular structures with lifetimes long enough to form entanglements[6]. Therefore the kinetics of this type of hydrogen bonds are to be localized below our transient entanglement in the Arrhenius plot (*Figure 6*). The end-to-end bonds or multimers[20] are able to form longer chain structures ($M_{eff} > M_c$) which can entangle, if the molecular weight of the original chains (oligomers) is high enough ($M_w > M'_w$)[6].

If we consider the time scale between the two types of hydrogen bond kinetic we have quasi stable end-to-end hydrogen bonds and no stable branched structures. For increasing molecular weights, the segmental concentration of the hydrogen bonded effective chains also increases and the influence of shorter chains decreases[5]. Therefore an entanglement can occur between the effective chains ($M_{eff} > M_c$) above a quasicritical molecular weight M'_w of the original PPG chains.

The location of the two types of hydrogen-bond in the diagram is crucial for our model, and more information about this would be useful.

CONCLUSIONS

In addition to previous ultrasonic and dynamic shear viscosity investigations[4,5], the results of our n.m.r. measurements give further evidence for the existence of entanglements between temporary associated chain structures ($M_{eff} > M_c$) formed by hydrogen end-to-end bonds of PPG chains having molecular weights in the range $M_c > M_w > M'_w \approx 1300$. The main argument for the indirect action of the hydrogen bonds is that the additional relaxation zone was found only for higher molecular weights $M_w > M'_w$, where the hydroxyl concentration is comparatively low, and that this relaxation vanished on destruction of the hydrogen bonds. The dielectric α′ relaxation and our additional *E* relaxation are assumed to have different activities in ultrasonic and n.m.r. measurements on the one hand and in dielectric measurements on the other hand. The α′ process is considered to be a normal mode effect, which seems to be nearly parallel to our additional process on the relaxation map.

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