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Polymer 41 (2000) 5305–5314

polymer

Dielectric study of the α-relaxation process evolution during polyurethane networks formation

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Received 12 April 1999; accepted 5 October 1999

Abstract

Quenched systems corresponding to different reaction extents of polyurethane (PU) network formation have been studied using broadband dielectric spectroscopy in order to apprehend the evolution of α-relaxation during gel formation. Three PU systems based on poly(oxypropylene) triol of molar mass 260, 700 and 6000 g/mol. have been investigated. While for the pure triols the distribution and temperature dependence of relaxation times are found to be similar, their evolution with connectivity in PU systems depends on molar mass of the triol used. This has been interpreted in terms of relative influence and transformation of active dipoles as a consequence of reaction and evidenced by the appearance of a new dynamic associated to new active dipoles. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyurethanes; Poly(oxypropylene) triol; Dielectric relaxation

1. Introduction

α-relaxation process has been studied experimentally in a wide range of polymers using different kinds of techniques such as mechanical [1,5–7], optical [2,5] and electrical [3]. This process associated with the glass transition and characterised by non-Arrhenius behaviour for associated relaxation times with non-Debye distribution results from local co-operative movements involving few repeating units of the polymer chain [4]. The relaxation times distribution width is usually found very large in polymeric systems [4]. Due to its wide frequency range, dielectric spectroscopy (DS) appears as a performing tool that allows the whole description of this process.

The present study concerns the evolution of the molecular dynamics during the formation of polyurethane (PU) systems based on poly(oxypropylene)triol (POP) of different molar masses and hexamethylene diisocyanate. Their preparation, their chemistry and also their physical properties are well defined and were the main interest of several studies [1,5–7]. Concerning the prepolymer, five relaxation processes have been already reported by dielectrics [9–14] in POP diols and triols of different molar masses. Three sub-T_g relaxation processes β, γ and δ have been pointed out and studied using different techniques. Above T_g, two relaxation processes have been reported: a normal mode process of a small magnitude at low frequency, which is observed only in POP of molecular weight higher than 1300 g/mol [12] and a segmental mode (α-relaxation) of large amplitude at high frequency which is less sensitive to variation in molecular weight. PU systems based on POP have been studied and the same relaxation processes have also been reported using different techniques such as rheology, ultrasonics [5,6], dynamic light scattering [5] and dielectrics [7,8]. Our attention, in this article, has been focused on the α-relaxation process and its evolution during gel formation. For the other relaxations (normal mode and secondary relaxations) more investigations are needed and so will be the subject of another paper. Real time dielectric measurements during PU formation are difficult to perform due to the relatively long time needed to collect data over the entire frequency and temperature ranges compared to the reaction time. For this reason, quenched PU samples corresponding to different steps of gel formation have been synthesised by varying the stoichiometric ratio.

A previous work [6,7] realised on the same systems using mechanical low and high frequencies revealed a continuous broadening of relaxation times distribution, while the temperature dependence of relaxation times is found to be independent on connectivity. As DS does not investigate the same phenomena in the same way as the mechanical one, one can expect some differences in the dynamics probed by the two experimental techniques. In DS experiment, the

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PII: S0032-3861(99)00734-X

Table 1
Triol characteristics

Triols	M_w (kg/mol)	Hydroxyl content (mol/g)
T260	0.26	11.58×10^{-3}
T700	0.73	4.135×10^{-3}
T6000	7.7	0.4795×10^{-3}

dipolar reorientation that provokes chain movements is responsible for relaxations [9] and hence the processes are not probed directly and depend on the position and the type of involved dipoles.

The plan of this paper is as follows. First, we will present and discuss the results obtained on triols of different molar masses used as precursors in PU formation. Secondly, an analysis of the evolution of α-relaxation process of the PU with stoichiometry in terms of distribution and temperature dependence of the relaxation times will be presented. A comparison among the three systems of different prepolymer mass will give a comprehension of how molar mass and connectivity influence the dynamics of α-relaxation of the PU networks.

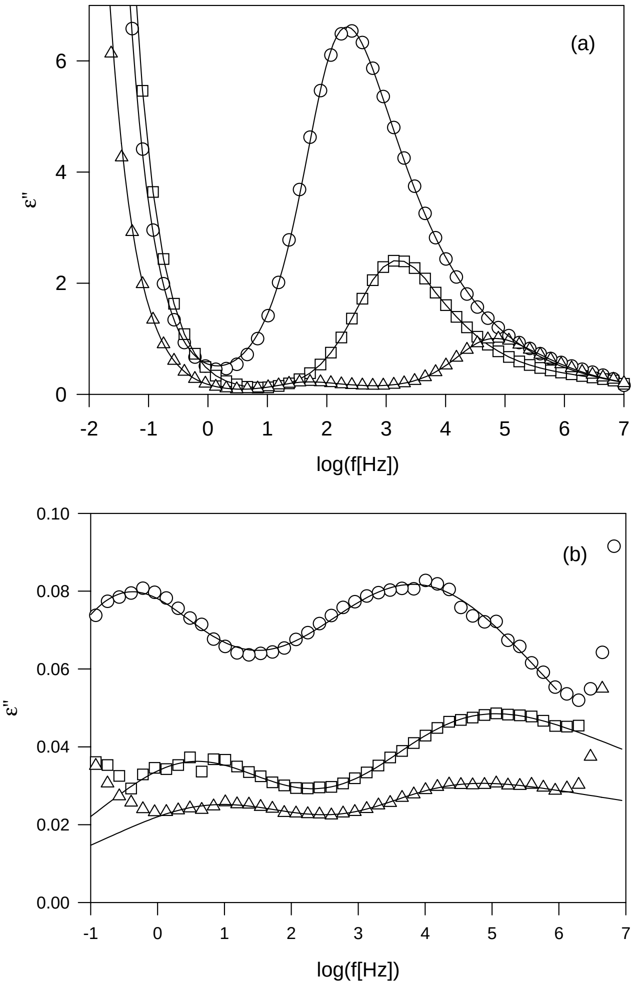

Fig. 1. Frequency dependence of the loss dielectric permittivity of T260 (○), T700 (□) and T6000 (△) at: (a) 233 K; and (b) 193 K. The solid lines represent fits to two HN functions plus conductivity in the case of (a).

2. Experimental

2.1. Samples

PU systems were synthesised by condensation of poly-(oxypropylene triol) with hexamethylen diisocyanate (HMDI). The polycondensation reaction catalysed by dibutyl tin dilaurate leads to a three-dimensional gel [15] if the two components are in a stoichiometric ratio. In order to study the system dynamics during its formation, quenched samples corresponding to different steps of reaction have been obtained by varying the stoichiometric ratio *r* that is defined as the initial ratio of the concentration of isocyanate groups [NCO] to that of hydroxyl groups [OH]. The stoichiometric ratios studied were the following: $r =$ 0.2, 0.4, 0.6, 0.8, and 1. The samples are prepared by mixing the dried triol with HMDI in the appropriate stoichiometry and the reaction was catalysed by addition of 2×10^{-3} g of dibutyltin dilaurate catalyst per gram of HMDI. To ensure complete reaction of isocyanate groups the samples were cured at 25°C for 24 h before measurements.

In order to apprehend the influence of molecular size on dynamic properties, three triols T260, T700 and T6000, of different molar mass (Table 1) are used. A gel is obtained for $r \geq r_c = 0.569$ in the case of PU systems based on T260 and T700 and $r \geq r_c = 0.76$ for the T6000. These critical stoichiometries have been determined experimentally using the solubility criteria. The observed deviation from Flory–Stockmayer is due to the average functionality of the triols which is not exactly equal to 3, and also due to the cyclisation effect.

2.2. Dielectric apparatus

The broadband DS equipment is from Novocontrol GmbH. It covers low frequency range (from 10^{-3} to 10^{7} Hz) and a large temperature range (133–673 K). For samples in the liquid state (e.g. $r < 0.6$), a special cell with gold electrodes is used. The solid samples are formed between two gold electrodes plates separated by two cylindrical quartz spacers of 50 μm diameter in order to ensure a constant thickness. The cell is placed inside a cryostat and the temperature is regulated with a nitrogen flow with an accuracy of ±0.01 K.

The analysis of isothermal dielectric spectra obtained over a wide temperature range from 133 to 373 K is performed using the empirical Havriliak–Negami (HN) function [17]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^\alpha]^\beta} + \frac{\sigma_0}{\varepsilon_0 \omega^n}$$

The fit parameters are the strength of the distribution

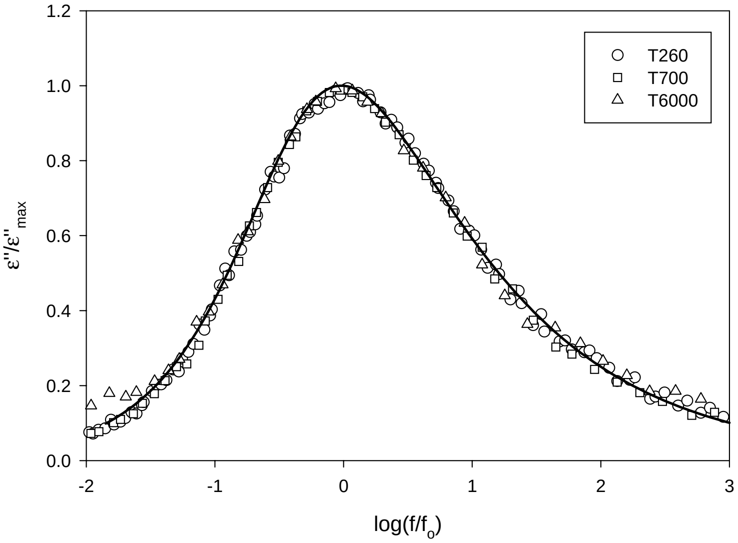

Fig. 2. Master curves of the loss dielectric permittivity for α-relaxation obtained on the pure triols. The solid line represents a fit to HN equation.

$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ with ε_∞ and ε_0 being, respectively, the high and low frequency limits of the relaxation process, the relaxation time τ and the coefficients α and αβ which represent, respectively, the low and high frequency slopes of $\varepsilon''(\omega)$ in a log–log plot. σ_0 represents the dc-conductivity and n an exponent. The fits are performed on master curves obtained at a reference temperature by superposition [16] of the dielectric loss ε''. This method allows us to point out a broadening of the relaxation process.

The temperature dependence of the characteristic relaxation times is analysed using Tamman–Vogel–Hesse–Fulcher (TVHF) law [18,19,20]:

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \qquad \text{with } \tau = \frac{1}{2\pi f_m}$$

where τ_0 is the relaxation time at very high temperature, B the apparent activation energy, T_0 the "ideal" glass transition temperature at which all movements are frozen and f_m is the frequency corresponding to the maximum of ε''.

3. Results and discussion

3.1. Relaxation processes in prepolymers

The dielectric spectra obtained over a wide temperature range on the different triols exhibit four well separated relaxation processes and a contribution of conductivity (Fig. 1a) reflected by the important increase of ε'' at low frequency. Below T_g, two well defined relaxations, β and γ are observed (Fig. 1b). Above T_g, two modes are active: the

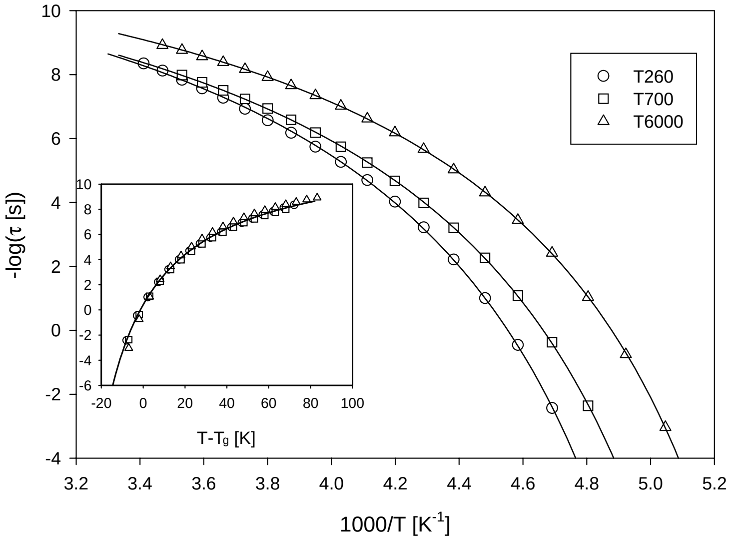

Fig. 3. Temperature dependence of the characteristic relaxation times of the segmental mode obtained on the pure triols. The solid lines represent a fit to TVHF equation. The enclosed graph represents the plots versus $T - T_g$ where T_g is the calorimetric glass transition temperature.

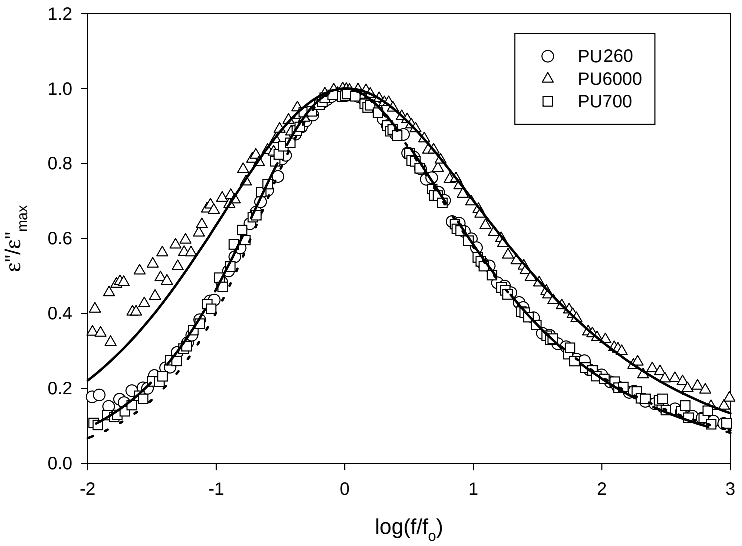

Fig. 4. Master curves of the loss dielectric permittivity for α-relaxation obtained on the Polyurethanes systems at the stoichiometry $r = 1$. The solid lines represent a fit to HN equation.

segmental mode (α-process) with high amplitude at high frequency associated with the glass–rubber transition and the normal mode of low magnitude at lower frequency which depends upon the molecular weight. The contribution to the dielectric strength arises from both OH dipoles situated at the chain ends and ether–oxygen dipoles situated in the main chain. It is well known [21] that the dipole relaxation of polyethers are both dipole components perpendicular and along the chain axis. The dominant one is the component perpendicular to the axis that will contribute to the segmental mode [22]. In addition, in certain cases the component along the axis has been shown to demonstrate characteristics of the normal mode of the polymer. This is the case for T6000 for which a well defined normal mode is observed as it was reported by several authors [10–14,23,24] for POP of molar mass higher than 1300 g/mol. Our main interest, in this paper, deals with the segmental mode associated to the glass–rubber transition. Master curves of the imaginary part ε'' (Fig. 2) obtained at a reference temperature showed that the shape parameters are not temperature dependent within the uncertainty due to the overlap of neighbouring processes. These parameters ($\alpha = 0.83$, $\beta = 0.51$) are also independent of molar mass. However, the parameter dielectric strength $\Delta\varepsilon$ exhibits a decrease with increasing molar mass:

$$\Delta\varepsilon = 1.48 + 6015/M_w$$

This is to be related with the concentration of OH dipoles, which is much more important for small molecules, while the ether–oxygen dipole concentration is almost constant and therefore its contribution to the α-process remains constant with varying molar mass; for very large molar masses the OH dipole contribution is negligible and one can expect a decrease of $\Delta\varepsilon$ toward the value due to the ether–oxygen as it was pointed out elsewhere [26]. So, it can be concluded that the contribution to α-relaxation is mainly due to the hydroxyl groups for T700 and T260 and to the ether–oxygen for T6000.

Although α-process is a segmental relaxation, the characteristic time depends upon molar mass as is shown in Fig. 3 where the temperature dependence of the relaxation time for the three triols is represented. The enclosed graph, representing the characteristic relaxation time as function of $T - T_g$, where T_g is the calorimetric glass transition temperature (Table 1), indicates that the effect of molar mass is an increase of T_g. The same TVHF parameters ($B = 539$, $\log(\tau_0) = -12.96$) can describe the temperature dependence of the prepolymers.

The α-relaxation process is found to be identical in terms of temperature dependence and distribution of relaxation times for all triols concluding that α-process is independent of molar mass [14]. Because the distribution and temperature dependence of the relaxation times for T260 and T700—which have, respectively, one propylene oxide (PO) and 4 PO segments per arm—is equal to that of T6000 with 40 PO per arm, we can conclude that the contribution to α-process arising from OH dipoles is not different from that of the ether–oxygen.

The question now is how the α-relaxation reported above will be influenced by the cross-linking reaction. In terms of dipolar transformation the reaction leads to a progressive disappearance of the OH dipole which is replaced by the urethane one. Complex interplay of effects associated with this transformation will result in changes of the relaxation process in terms of distribution and temperature dependence of the relaxation time.

3.2. Polyurethane networks

In Fig. 4 we show master curves of the dielectric loss

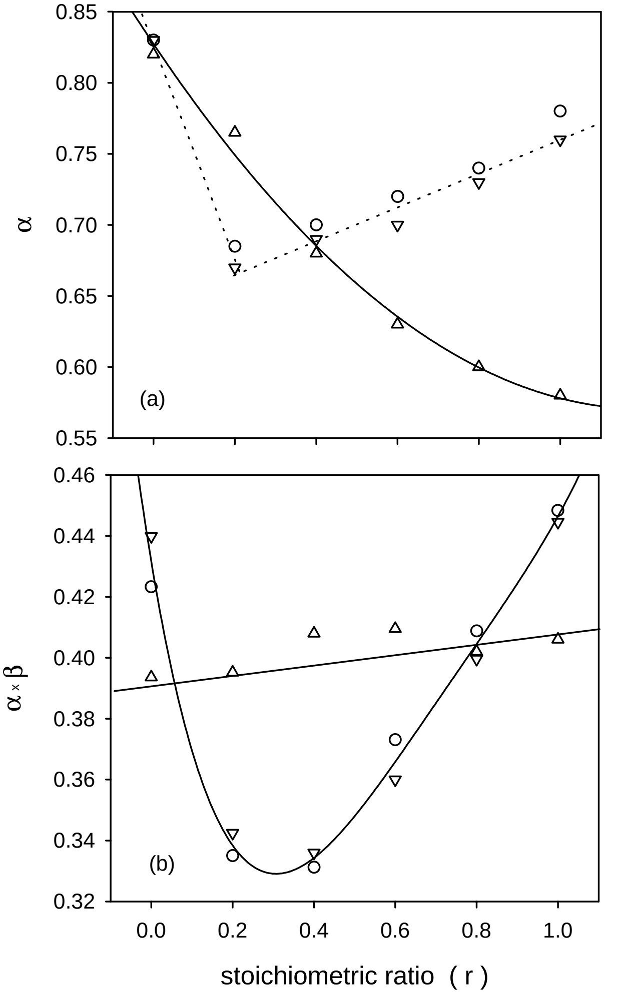

Fig. 5. Representation of the evolution of: (a) Havriliak–Negami α_{HN}; and (b) $\alpha_{HNx} \times \beta_{HN}$ coefficients versus stoichiometry r for the different systems: PU260 (▽); PU700 (○); and PU6000 (△).

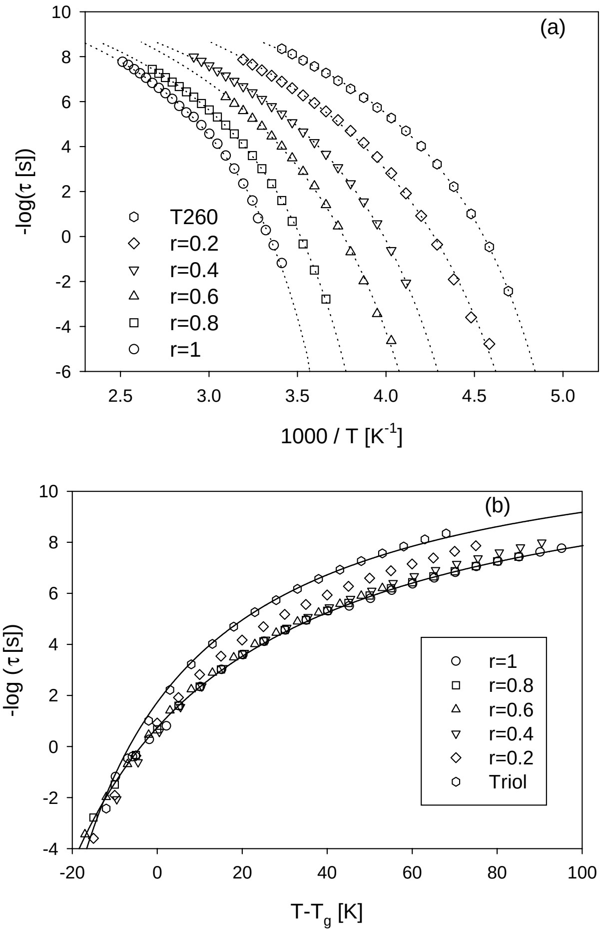

Fig. 6. Temperature dependence of the characteristic relaxation times of the segmental mode obtained on PU260 systems at different stoichiometries as function of: (a) inverse temperature; and (b) $T - T_g$. The solid lines represent a fit to TVHF equation.

obtained at a reference temperature on PU260, PU700 and PU6000 at $r = 1$. Unexpected broadening is observed in the case of PU6000 compared to PU260 and PU700 for which distributions are identical. Distribution parameters of both systems present the same behaviour (Fig. 5a and b) versus stoichiometric ratio: they pass through a minimum which appears close to $r = 0.3$ for $\alpha\beta$ and before $r = 0.2$ for α. The minimum is sharper in the case of α coefficient. This minimum seems to appear as soon as urethane bonds are formed. Other studies have to be made in order to determine the exact value of this minimum. Above the minimum, α presents a linear increase with r.

For the PU6000 system a continuous decrease of α and an increase of $\alpha\beta$ (Fig. 4a and b) are observed. Despite the uncertainties due to the overlap of the normal mode, which does not exist in the other systems, the evolution of the distribution parameters with the reaction extent for PU6000 is different from that of PU260 and PU700. We have seen earlier that the segmental mode in T6000 is mainly due to the ether–oxygen dipole as the concentration of OH groups is very low. Hence, one can expect the distribution parameters to remain constant with stoichiometry in the case of PU6000 as only OH dipoles are transformed to urethane during the reaction. A fit corresponding to this hypothesis has been performed and is found to be equivalent to the fit using free parameters [27] for system at $r = 0$ and $r = 1$. The parameters found for PU260 and PU700 (which are almost the same) have also been tested [27] but give incorrect fits. It is then concluded that for high molar masses, the effect of structure changes is negligible as α-relaxation proceeds mainly from ether–oxygen dipoles that are not modified during gel formation.

In terms of temperature dependence, the relaxation times are well fitted to the TVHF law and the curves for different stoichiometries r are presented in an Arrhenius plot for the different systems in Figs.6a, 7a and 8a. It can be seen that for PU systems based on high molar mass the TVHF curves are closer. This is to be related with the glass transition temperature. DSC experiments (Table 2) have been made in order to determine whether the glass transition temperature (T_g) is responsible for such behaviour. For PU6000 systems a perfect superposition of the curves is obtained when plotted versus $T - T_g$: the relaxation times follow a same TVHF law which is not the case for PU260 and PU700 systems. The deviation is higher for low stoichimetries. In the gel state ($r \geq 0.6$) a nearly good superposition is obtained. A comparison has been made between fully reacted systems ($r = 1$) (Fig. 9). It can be pointed out that PU260 and PU700 obey to the same TVHF law different from that of PU6000 indicating that the molecular dynamics associated with urethane dipoles is different from that associated with ether–oxygen dipole as the latter is predominant in PU6000.

Detailed examination of the dielectric spectra for PU260 system at $r = 0.2$ revealed a broadening with increasing temperature and at high temperatures two separated peaks are observed so that two HN functions are needed to fit the data well. This double peak appearing at high temperatures and high frequencies has been verified using high frequency DS (Fig. 10). The appearance of the second peak is responsible for the sudden broadening of the α-relaxation at low frequency and temperature and a non superposition of TVHF plots for the stoichiometries below 0.6. We first supposed that this was due to the secondary relaxations that merge into α-relaxation at high temperatures but this was not the case. A fit using two HN functions has been performed in the case of sample PU260 at $r = 0.2$ at different temperatures. We show in Fig. 11 both relaxation times with those of T260 and PU260 at $r = 0.8$ as function of $T - T_g$. The superposition of the low and high frequency with, respectively, PU260 ($r = 0.8$) and T260 indicates that two different dynamics are probed.

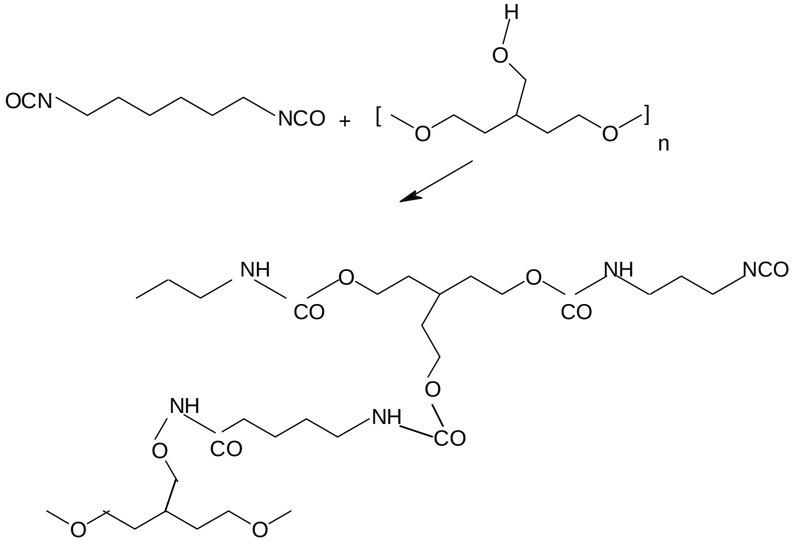

Table 2
Glass transition temperature of polyurethane samples

Polyurethanes	Triols	$r = 0.2$	$r = 0.4$	$r = 0.6$	$r = 0.8$	$r = 1$
PU260	T221	234	248	264	282	303
PU700	T215	225	233	242	250	260
PU6000	T205	211	214	215	215	215

Examination of the dipole change operating during network formation may provide explanations about the two dynamics probed. The increase of reaction extent leads to the progressive disappearance of the OH dipoles that are replaced by urethane ones leading to the formation of new species of molecules such as dimers and trimers. Chromatographic experiments (Fig. 12) performed on samples in the liquid state indicate a maximum distribution of the smallest species (monomers, dimers and trimers) for a stoichiometric ratio $r \sim 0.2$ close to the minimum value of the HN distribution parameter α. At the critical stoichiometric ratio r_c an infinite size cluster is formed and above r_c the remaining smallest species will progressively connect to the giant cluster. In the final material ($r = 1$) all the OH are replaced by urethane links and the α-process proceeds mainly from urethane dipoles.

Between these two values of r, the relaxation time distribution varies with r. The broadening seems to be correlated to the mass distribution of species. An experiment carried out on a mixture of T260 with T700 at two concentrations showed that only one α-relaxation is probed, whose frequency depends on the concentration in contrary to the relaxation time distribution which remains constant (Fig. 13). The result is not surprising, as only one dipole type is active predominantly. PU260 system, at $r = 0.2$, could be considered as a mixture of 50% of T260, 28% of dimers and 18% of trimers and other species whose concentration can be neglected. The difference with the mixture of two pure triols of different molar masses is the presence of the active urethane dipoles that are then responsible of the second relaxation probed. In addition, the values of strength $T \times \Delta\varepsilon$ are almost constant with r [27], which means that the

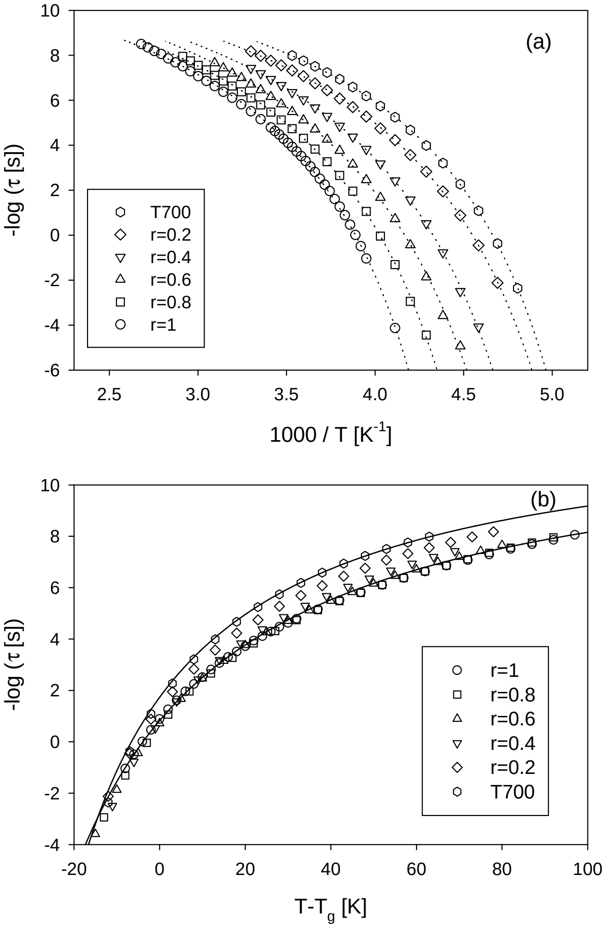

Fig. 7. Temperature dependence of the characteristic relaxation times of the segmental mode obtained on PU700 systems at different stoichiometries as function of: (a) inverse temperature; and (b) $T - T_g$. The solid lines represent a fit to TVHF equation.

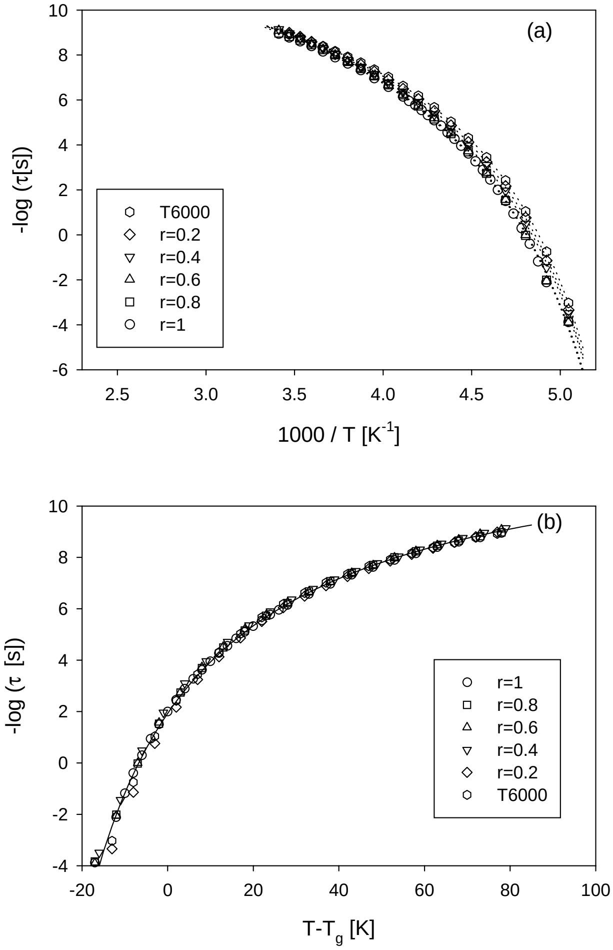

Fig. 8. Temperature dependence of the characteristic relaxation times of the segmental mode obtained on PU6000 systems at different stoichiometries as function of: (a) inverse temperature; and (b) $T - T_g$. The solid lines represent a fit to TVHF equation.

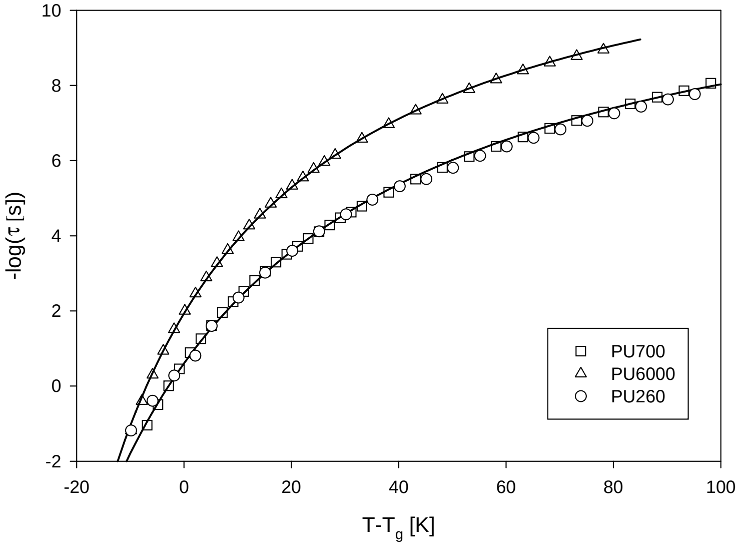

Fig. 9. Temperature dependence of the characteristic relaxation times of the segmental mode obtained on the PU systems for the stoichiometry $r = 1$ versus $T - T_g$.

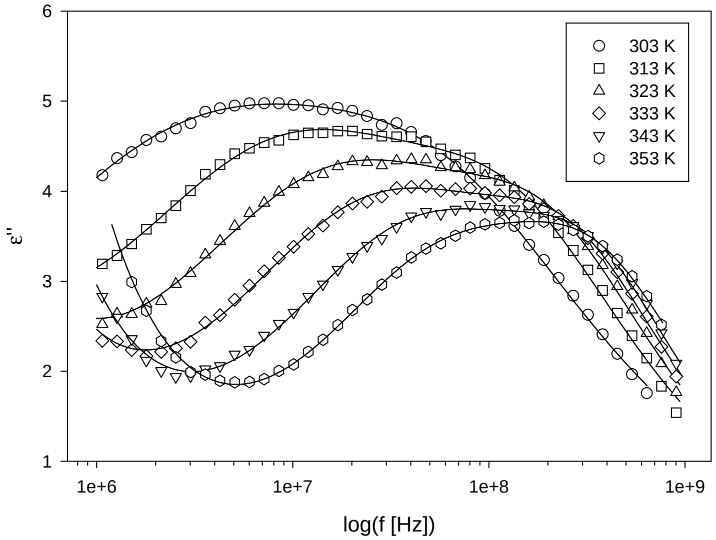

Fig. 10. Frequency dependence of the loss dielectric permittivity at high temperature and frequency obtained in the case of PU260 at $r = 0.2$. The solid line represent a fit to a sum of two HN functions plus conductivity.

dipole moment per segment [25] should be similar for both kind of dipoles. A calculation gives a value of 2.5 D for the dipole moment of the isolated urethane function (e.g. *N*-methyl methyl carbamate), in agreement with measurement on ethyl carbamate [28] of similar structure (2.59 D). When considering the whole polymer, this value has to be lowered due to atoms chain influence.

Finally, two relaxation processes are in competition, one linked to hydroxyl dipole and the second to urethane dipoles. In the case of PU260, at $r = 0.2$, the two relaxations are well separated while for the other systems they result in a simple broadening. With increasing r the transformation of OH groups to urethane dipoles leads to a lowering of the process linked to OH dipole. At $r > 0.6$ the urethane dipoles are predominant so that only one dynamics is observed. This is confirmed by the superposition of the TVHF plots for these stoichiometries.

PU systems based on POP belong to a special class of systems for which the distribution parameters value depends on the technique used as it was pointed out elsewhere [29]. Previous works [6,7] made on the same system with high and a low frequency mechanical measurement gives a continuous broadening of the relaxation time distribution. In terms of temperature dependence, a perfect superposition of TVHF plots is obtained by a temperature shift equal to the calorimetric T_g implying constant values of B and τ_0 with r. The influence of stoichiometric ratio appears only as an

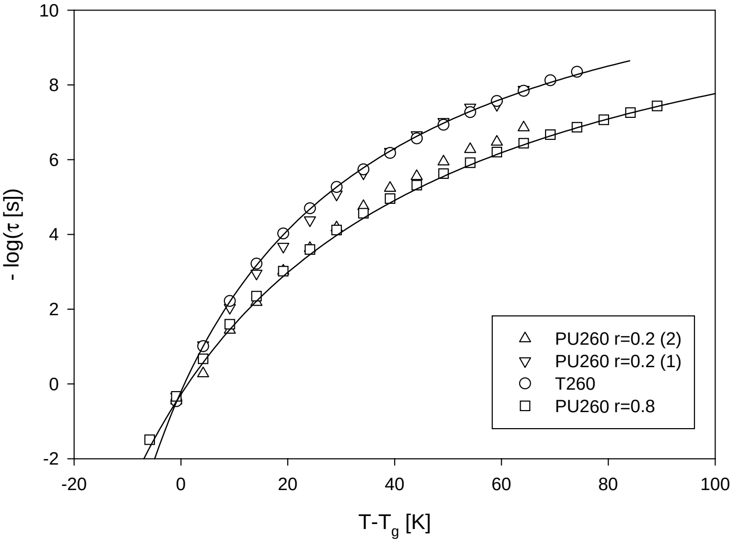

Fig. 11. Temperature dependence of characteristic relaxation times obtained on PU260 ($r = 0.2$ and $r = 0.8$) and T260 as function of $T - T_g$. The two relaxation times of PU260 ($r = 0.2$) were obtained by a simultaneous fit of storage and loss dielectric permittivity to a sum of two HN function.

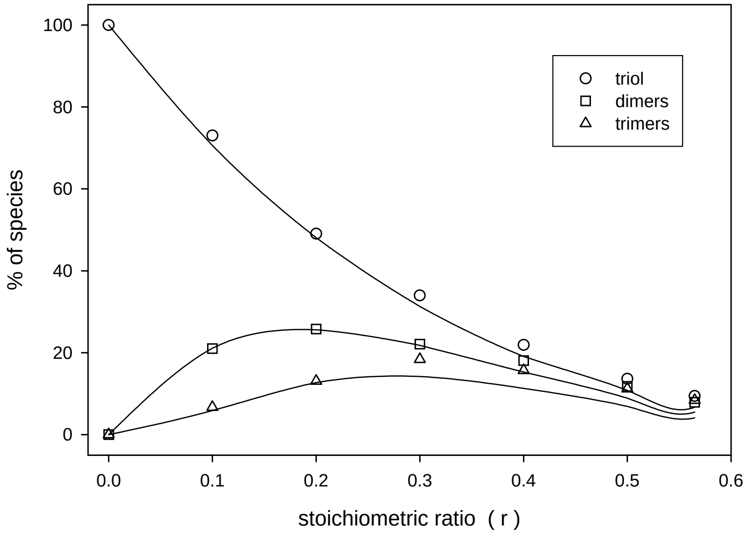

Fig. 12. Percentage of monomers, dimers and trimers at different stoichiometries obtained on PU700 systems by size exclusion chromatography.

increase of T_0 values. For dielectric measurements, The distribution and TVHF parameters depend on the dipoles type involved in the relaxation process and their position in the chain.

4. Conclusion

PU systems are interesting materials to apprehend dynamical properties in polymers as they can be considered as models for network formation study. Low frequency (10^{-2}–10^{7} Hz) dielectric measurements have been performed on three PU systems based on POP triols of different molar masses. In order to evaluate structure changes influence during network formation on α-relaxation process, quenched samples representing different cross-link extents have been obtained by varying the stoichiometric ratio r.

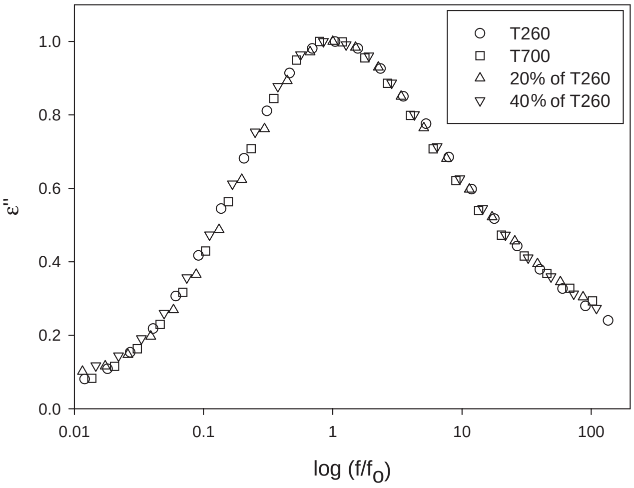

Fig. 13. Superposition of loss dielectric permittivity obtained on mixtures of T260 and T700 at different concentrations of T260.

Comparison of the evolution of the relaxation spectra between the three systems in terms of distribution and temperature dependence of relaxation times revealed two different behaviours.

A maximum broadening is observed at $r = 0.2$ for the systems PU260 and PU700 based on low molar mass prepolymer and for high molar mass system (PU6000) a continuous and slight decrease is noticed despite the similar distribution characterising the prepolymers.

The temperature dependence of PU6000 is quite constant with r and a temperature shift equal to T_g allows a perfect superposition whereas for PU260 and PU700 no superposition has been obtained. It can be noticed that for the prepolymers, the same TVHF parameters can describe the temperature dependence of the characteristic relaxation times.

Considerations on dipole transformation occurring with increasing reaction extent lead to the conclusion that two close dynamics are in competition during gel formation in the PU260 and probably in PU700: the first one is associated to OH dipoles and is predominant for systems of $r < 0.6$ and the second one is due to the urethane dipoles. This conclusion is evidenced by the observation of a second peak at high temperature in the system PU260 at $r = 0.2$. The ether–oxygen dipoles that are of constant contribution in all systems are not transformed during the reaction. In PU6000, these dipoles are predominant as the concentration of OH dipoles is negligible, explaining the non-evolution of the TVHF plots and distribution parameters with r.

The evolution of α-relaxation process during gel formation as studied by DS is completely different from that pointed out by mechanical high and low frequency studies. The differences are accounted to the fact that dielectric relaxation is probed through the dipoles movement and hence depends on the number of active dipoles and their position in the chain.

Acknowledgements

We wish to thank Prof P. Pissis from National Technical University of Athens, Greece, for helpful discussion and L. Fontaine for dipole moment calculation.

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