Polymer Bulletin 18, 39–45 (1987)

Polymer Bulletin

© Springer-Verlag 1987

Viscosity and relaxation times temperature behaviour above the glass transition in some glassy polymers

J. M. Alberdi, A. Alegría, E. Macho, and J. Colmenero*

Departamento de Física, Facultad de Química, Universidad del País Vasco,
Apdo. 1072, E-20080 San Sebastián, Spain

Abstract

We have performed mechanical and dielectric dynamic measurements above the glass-transition temperature range of two glassy-polymers: Poly(Hydroxyether of Bisphenol-A) and Poly(Carbonate of Bisphenol-A). From these measurements the temperature dependence of mechanical and dielectric mean relaxation times has been calculated. Results obtained have been compared with the viscosity temperature behaviour of the same polymers, which has been reported elsewhere. Both, relaxation times and viscosity temperature behaviour can well be described by Doolittle functional forms, $\exp\{1/[\alpha_f(T-To)]\}$, with the same values of To but different values of the apparent free-volume expansion coefficient, α_f. This difference in the experimental behaviour has been addresed in the framework of the free-volume model ideas. In this context, the different values of α_f obtained from viscosity and relaxation times temperature behaviour can be understood assuming different values of critical volume controlling the molecular motions associated to viscosity and relaxation processes. Similar conclusions have also been obtained by means of a fine revision of the viscosity and relaxation times data of another two glassy-polymers: Poly(Arylate) and Poly(Sulfone of Bisphenol-A), reported previously.

Introduction

Above the glass-transition temperature range, a glassy polymer is in a metastable thermodynamic equilibrium state. The molecular transport mechanisms in such a system, as well as the nature of the glass-transition, are related problems that still remain unsolved. From an experimental point of view, the main characteristic magnitudes of molecular transport are, the newtonian viscosity and the time scales associated to the different relaxation techniques, as for example mechanical and dielectric relaxation spectroscopies. There is not up to now a fundamental theory of the temperature behaviour of newtonian viscosity in polymeric systems. Arrhenius-type forms with activation energy values depending on the experimental temperature range and, more recently, power law expressions have been often used to parametrize much experimental viscosity data. However, the most widely extended expression is the so-called Vogel-Fulcher or Doolittle law which has been theoretically justified in the framework of the free-volume model (1). On the other hand, the temperature dependence of the different empirical relaxation times is also frequently fitted by Arrhenius or Doolittle equations. In this framework, a key question is to know if the relaxation times, obtained from very different relaxation probes and newtonian viscosity, behave with temperature in a similar way, i.e., are these different phenomena driven by a single microscopic mechanism?.

---

* To whom offprint requests should be sent

In this line, a different temperature behaviour for the viscosity and short time viscoelastic mechanisms above the glass-transition of a Polyestirene (PS), a linear Poly(vinyl acetate) (PVAc) and an atactic Polypropilene have recently been reported (2-4). This difference in behaviour has also been addressed in the context of several theoretical approaches to molecular motions and relaxations in polymer glasses (2,4).

In a recent paper (5), however, with only one Doolittle equation, we have described viscosity and both, dielectric and mechanic relaxation times temperature behaviour above the glass-transition of two commercial glassy polymers: Poly(Arylate) (PAr) and Poly(sulfone of Bisphenol-A) (PSF). Going into these questions, we have performed, in this paper, dielectric and mechanical dynamic measurements on another two glassy polymers: Poly(Hydroxyether of Bisphenol-A) (PH) and Poly(carbonate of Bisphenol-A) (PC). The measurements corresponding to PAr and PSF, reported in ref. 5 have also been revised and discussed.

Experimental

Commercial polymers, Phenoxy (PKHH from Union Carbide) and Polycarbonate (Macrolon 2800 from Bayer) have been used in this work. The average number and viscous molecular weight of these polymers were, $\overline{M}_n$ = 25000 and $\overline{M}_w$ = 80000 for Phenoxy and $\overline{M}_n$ = 17000 and $\overline{M}_w$ = 26000 for Polycarbonate.

Sheet stocks 0.6 mm thick were formed by pressing in an air atmosphere by a Schwabenthan Polystat 200 T press at 54 atm and 470 K for PH and 520 K for PC. For dielectric and mechanical measurements 12 mm diameter discs and rectangles of 12x30 mm^2 were respectively cut from the sheets.

Viscosity measurements used in this work have been reported in a previous paper (6). They were performed by the squeeze flow between parallel plates technique. The experimental viscosity range covered by this technique was 10^5 to 10^{10} P.

AC dielectric measurements in the frequency range $10\text{-}10^6$ Hz were performed, at a fixed frequency, during heating at a rate of 6 K/min. Both, real and imaginary parts of the dielectric constant were measured as a function of temperature. The experimental system used by us has already been described in previous works (7).

Dynamic mechanical measurements were also performed at a fixed frequency during heating at a rate of 2 K/min. A standard Polymer Laboratories DMTA apparatus which works in a frequency range between 0.1 and 100 Hz was used.

Results and Discussion

From AC dielectric and dynamic mechanical measurements, both, dielectric, τ_D, and mechanical, τ_M, mean relaxation times were obtained taking respectively, $\omega \times \tau_D = 1$ and $\omega \times \tau_M = 1$ at the temperature of dielectric and mechanical tangent loss maxima. The frequency range used by us allows to obtain τ_D values between 10^{-2} and 10^{-8} seconds and τ_M values between 1 and 10^{-4} seconds.

Viscosity values, $\eta(T)$, used in this work were reported in ref. 6. They were fitted by Doolittle expression

$$\eta(T) = \eta_o \exp[\frac{b}{\alpha_f^*(T-To)}] \qquad [1]$$

where η_o is a preexponential factor, α_f^* is the expansion coefficient of the free volume, To is the temperature at which free volume vanishes and b is a numerical factor of order unit. The values of the free - volume parameters, apparent free-volume expansion coefficient $\alpha_{f\eta} = \alpha_f^*/b$ and To, were obtained from those fits (6).

In order to compare the temperature behaviour of viscosity, η, and relaxation times, τ_D and τ_M, we have introduced the non-dimensional scaled magnitudes $\varphi_\eta(T)$, $\varphi_D(T)$, and $\varphi_M(T)$ as,

$$\varphi_\eta(T) = \log_{10} \frac{\eta(T)}{\eta(Tr)} \; ; \quad \varphi_D(T) = \log_{10} \frac{\tau_D(T)}{\tau_D(Tr)} \; ; \text{and} \quad \varphi_M(T) = \log_{10} \frac{\tau_M(T)}{\tau_M(Tr)} \qquad [2]$$

where Tr is a reference temperature which has been chosen for each polymer in the common temperature range to both viscosity and relaxation time measurements. This procedure implies the assumption that scaled magnitudes $\varphi_\eta(T)$, $\varphi_D(T)$, and $\varphi_M(T)$ take the same value at Tr. Values of Tr chosen as well as the values of η, τ_D and τ_M at these reference temperatures are shown in Table I.

Table I: Values of the reference temperature and corresponding viscosity and relaxation times for the four polymers investigated.

Polymer	Tr (K)	η(Tr) (P)	τ_D(Tr) (s)	τ_M(Tr) (s)
PH	396	10^8	8×10^{-6}	8×10^{-5}
PC	440	3×10^8	5×10^{-5}	5×10^{-4}
PSF	490	10^8	8×10^{-6}	------
PAr	500	3×10^8	2×10^{-5}	------

Figures 1 to 4 show the $\varphi_\eta(T)$, $\varphi_D(T)$, and $\varphi_M(T)$ behaviour corresponding to PH, PC, PSF and PAr plotted versus 1/(T - To). As can be seen, $\varphi_D(T)$ and $\varphi_M(T)$ have an approximately linear behaviour as a function of 1/(T - To), indicating that To value deduced from viscosity measurements, also applies for mechanical and dielectric relaxation data. Moreover, φ_D and φ_M behave in a similar way with temperature suggesting that mechanical and dielectric relaxations are driven by the same mechanism. This last result has already been reported for other polymers (8). However, the linear behaviour of φ_D and φ_M have a different slope to the corresponding one of φ_η. This implies apparent free-volume expansion coefficient, different to $\alpha_{f\eta}$ for the relaxation times behaviour. Values of this apparent free-volume expansion coefficient deduced from Fig. 1 to 4 which we will term $\alpha_{f\tau}$, are shown in Table II together with $\alpha_{f\eta}$ and To values taken from ref. 6.

From the results described above we can conclude that the temperature variation of viscosity and relaxation times above the glass-transition temperature of PH, PC, PSF and PAr, is different although in some cases (mainly in the case of PAr) the temperature behaviour of both kinds of magnitudes can well be parametrized by only a single set of Doolittle parameters (5).

Similar results have been obtained by Plazek et al. for Polyestirene (PS), a linear Poly(vinyl acetate) (PVAc) and an atactic Polypropilene, as has been commented in the introduction. Different explanations of this behaviour have been suggested by these authors over recent years. In 1982 (2) they fit viscosity and relaxation time temperature behaviour with only one free-volume functional form but different from the Vogel-Fulcher or Doolittle one. Later (3,4) they suggested that viscosity and relaxation times temperature behaviour could be associated to two different fractional free volumes. In addition, they assumed the same fractional free-volume expansion coefficients and different To (called T_∞ by them). Finally (4) they have applied to this problem the Ngai

TableII: Free volume expansion coefficients correponding to viscosity ($\alpha_{f\eta}$) and relaxation times ($\alpha_{f\tau}$) as obtained from Fig. 1 to 4.

Polymer	To (K)	$\alpha_{f\eta} \times 10^4$ (K^{-1})	$\alpha_{f\tau} \times 10^4$ (K^{-1})	$b\tau/b\eta$
PH	311	8.3	4.6	1.8
PC	349	5.6	3.2	1.8
PSF	387	5.9	3.1	1.9
PAr	415	8.2	7.4	1.1

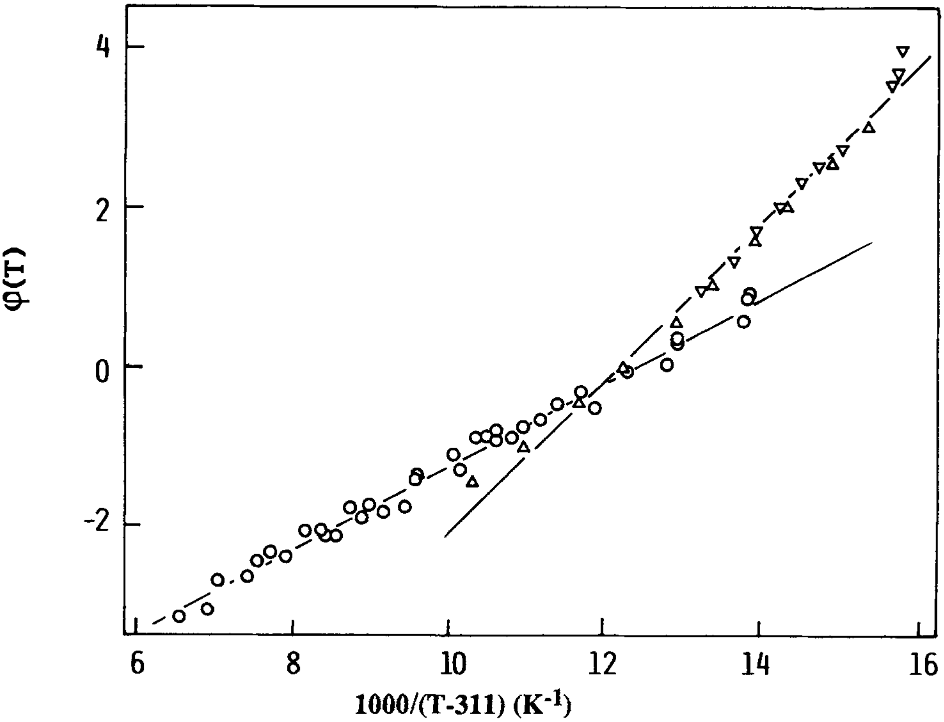

Fig. 1: φ(T) versus 1000/(T-To) for PH. (o) viscosity (ref. 6); (Δ) dielectric relaxation time; (∇) mechanical relaxation time.

coupling model for relaxation (9). From this application they concluded that viscosity and relaxation times behave as different processes but both related to the same microscopic mechanism, in this case, this mechanism is the primitive friction factor for the primary segmental relaxation. Different temperature behaviour of viscosity and relaxation times emerges through the coupling parameter, *n*, which can be viewed as a measure of the complexity of the molecular motions involved in the observed process. Values of *n* deduced from relaxation time behaviour ($n \approx .65$) are greater than those deduced from the viscosity one ($n \approx .45$).

However, the difference observed in behaviour of viscosity and relaxation times can easily be explained taken into account the free-volume model ideas (1). In this framework the parameter b of equation [1] can be expressed as

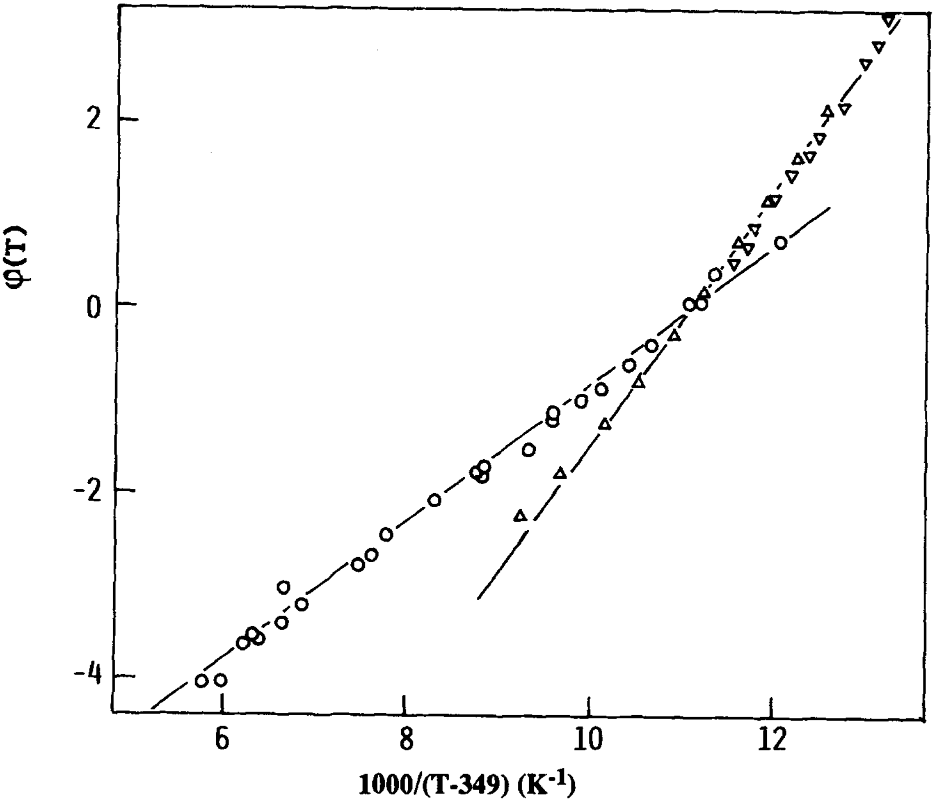

Fig. 2: $\varphi(T)$ versus $1000/(T\text{-}To)$ for PC. (o) viscosity (ref. 6); (Δ) dielectric relaxation time; (∇) mechanical relaxation time.

$b=\gamma V_f^*/V$ where V is a volume of normalization, γ a geometrical factor close to unit and V_f^* is the critical volume controlling the molecular transport. As has already been commented the apparent free-volume parameters, which can be deduced from the experimental behaviour of $\eta(T)$, $\tau_D(T)$ and $\tau_M(T)$ are α_f^*/b and To (Eq. [1]). Thereby, different values of the apparent free-volume expansion coefficient obtained from viscosity or relaxation times temperature behaviour can be understood assuming different values of b, i.e., different values of critical volume V_f^* but the same free-volume expansion coefficient α_f^*. With these assumptions we can calculate, from the values of $\alpha_{f\eta}$ and $\alpha_{f\tau}$, the values of $b\tau/b\eta$ (see Table II). As can be seen $b\tau$ is about twice $b\eta$ except that for PAr where $b\tau$ is about of $b\eta$.

In this picture, viscosity and relaxation times temperature behaviour are described by means of Doolittle equations depending on the fractional free-volume in the sample which is univocaly defined as $f=\alpha_f^*(T\text{-}To)$. However, the critical volume for molecular motions involved in viscosity and relaxations processes becomes different. Theses results are in good agreement with the assumed idea that motions involved in viscous flow should be coaxial with the polymeric chain while those associated to relaxation behaviour should be normal to the backbone. Therefore, viscous motions (coaxial) would require smaller critical free volumes.

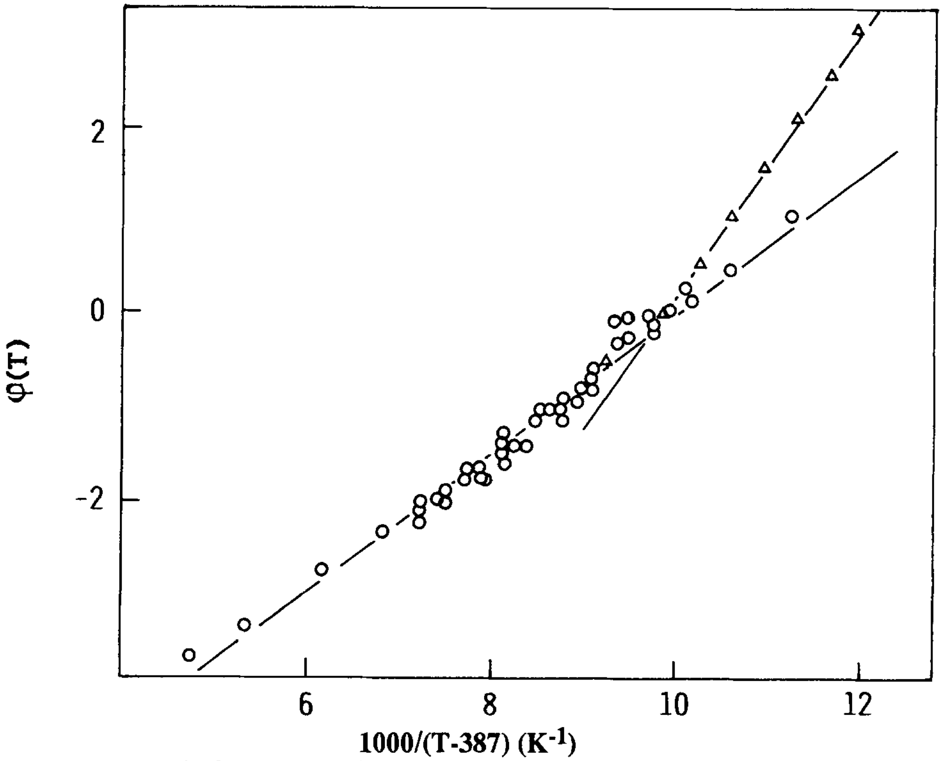

Fig. 3: φ(T) versus 1000/(T-To) for PSF. (○) viscosity (ref. 6); (Δ) dielectric relaxation time (ref. 5)

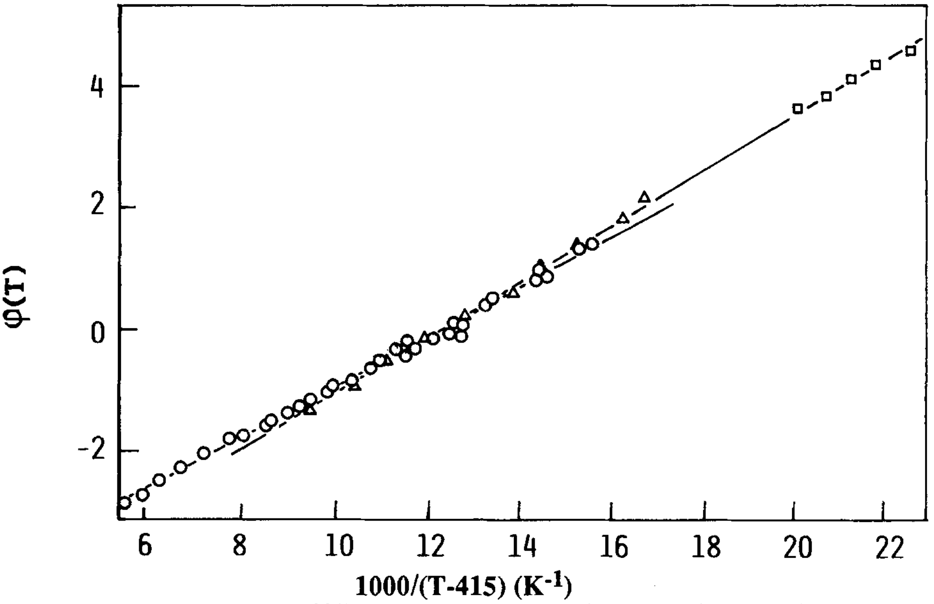

Fig. 4: φ(T) versus 1000/(T-To) for PAr. (○) viscosity (ref. 6); (Δ) dielectric relaxation time; (□) enthalpic relaxation time (ref. 5).

On the other hand, this simple kind of interpretation results compatible with the coupling model ideas because a greater critical free-volume would involve a greater complexity of the observed process, i.e. a greater value of the coupling parameter, *n*, as is experimentally observed.

Acknowledgments

This work was supported in part by CAICYT Project n° 1093/84.

References

1. M.H. Cohen and D. Turnbull, J. Chem. Phys. 31, 1164 (1959).
2. D. J. Plazek, J. Polym. Sci., Polym. Phys. Ed. 20, 729 (1982).
3. D.L. Plazek and D.J. Plazek, Macromolecules 16, 1469 (1983).
4. K.L. Ngai and D.J. Plazek, J. Polym. Sci. Polym. Phys. Ed 24, 619 (1986).
5. J.M. Alberdi, A. Alegría, E. Macho, and J. Colmenero, J. Polym. Sci., Polym. Lett. Ed. 24, 399 (1986).
6. E. Macho, A. Alegría, and J. Colmenero, Polym. Eng. Sci. (in press)
7. A. Alegría, J. Colmenero, J.J. del Val, and J.M. Barandiarán, Polymer 26, 913 (1985).
8. N.G. McCrum, B.E. Read and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, Wiley, New York, (1967).
9. K.L. Ngai, Comments Solid State Physics 9, 127 (1979) and 9, 141 (1980).

Accepted May 24, 1987 C