ELSEVIER

Polymer 42 (2001) 8907–8910

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Dielectric relaxations of poly(2-norbornyl methacrylate) and poly(3-methyl-2-norbornyl methacrylate)

R. Díaz-Calleja[a,*], A. García-Bernabé[a], C. Pagueguy[b], L. Gargallo[b], D. Radic[b]

[a]Departamento de Termodinámica Aplicada, Universidad Politécnica de Valencia, Apartado 22012, E-46071 Valencia, Spain
[b]Departamento de Química Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile

Received 23 February 2001; received in revised form 21 May 2001; accepted 29 May 2001

Abstract

Dielectric behaviour of poly(2-norbornyl methacrylate) (P2NBM) and poly(3-methyl-2-norbornyl methacrylate) (P3M2NBM) was studied. The effect of the methyl substituent on the norbornyl ring is to decrease the temperature of the dynamic glass transition about 50 K. Moreover, weak secondary relaxations are observed in the two polymers under study. The secondary process of P3M2NBM has been conveniently analysed in terms of the empirical Fuoss–Kirkwood (F–K) equation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric relaxations; Poly(2-norbornyl methacrylate); Poly(3-methyl-2-norbornyl methacrylate)

1. Introduction

Under electric perturbative force fields, polymers containing saturated cyclic side chains exhibit considerable dielectric activity [1–5]. These kinds of polymers show well-defined relaxations in the glassy state that have been attributed to the chair-to-chair conformational transition in the ring. The substitution in the ring by different groups allow to monitoring the molecular motions of the chain and by this way, it is possible to get information about the dynamics of conformational changes in these polymers [6,7]. In fact, the substitutions in the ring by *tert*-butyl groups in poly(cyclohexyl methacrylate) show that the relaxation processes are strongly dependent on the position of the substituent [8]. The insertion of polar groups is another way to enhance dielectric activity in polymers. Recently, we have reported results dealing with the effect of spacer groups on dynamic mechanical and dielectric behaviour of poly(cyclohexyl alkyl methacrylates) [9] and poly(methacrylates) [10] containing different rings in side chain. The conformational dynamics of these polymers can be controlled depending on the structure, nature and bulkiness of the substituents. The bulkiness of the side chain enhances the stiffness of the polymer chain and a decrease in the relaxation strength of the sub glass relaxations. However, differences in the relaxational behaviour of these kinds of polymers should be experimentally detected when appropriate substituents are inserted in the side chain.

The aim of this work is the study of the dielectric relaxational behaviour of polymers with saturated rings in the side chain and restricted conformational dynamics. Comparison of the dielectric behaviour of two polymers with slightly structural differences in the side ring, i.e. poly(2-norbornyl methacrylate) (P2NBM) and poly(3-methyl-2-norbornyl methacrylate) (P3M2NBM) (see Scheme 1) will be carried out.

2. Experimental

2.1. Monomer and polymer preparation

2-Norbornyl methacrylate (2NBM) and 3-methyl-2-norbornyl methacrylate (3M2NBM) were obtained by reaction of methacryloyl chloride with the corresponding alcohols in toluene using triethylamine as acid acceptor, following a procedure previously reported [11–14]. Monomers were polymerised under vacuum, in toluene solutions at 323 K using α,α'-azo-bisisobutyronitrile as initiator. Polymers were purified by successive reprecipitations with methanol. Samples were vacuum dried at 303 K during several days.

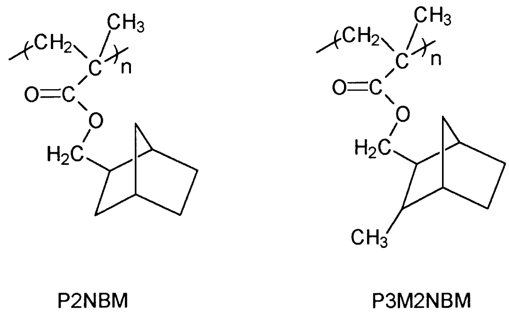
2.2. Dielectric measurements

The real and imaginary parts of the complex dielectric

---

* Corresponding author.
E-mail address: rdiazc@ter.upv.es (R. Díaz-Calleja).

0032-3861/01/$ - see front matter
PII: S0032-3861(01)00369-X



Scheme 1.

permittivity ϵ^* were measured in dry nitrogen atmosphere with a DEA 2970 apparatus from TA Instruments. The thermal history was a multiplexing one from -130 to 250°C at a rate of 1°C/min and 26 frequencies were used in the range of 10^{-1}–10^5 Hz.

3. Results and discussion

In Figs. 1 and 2, the isochronal curves of the permittivity and loss factor of P2NBM and P3M2NBM are shown as a function of temperature at fixed frequencies. Only three selected frequencies were used for sake of clarity. A prominent relaxation associated with the dynamic glass transition

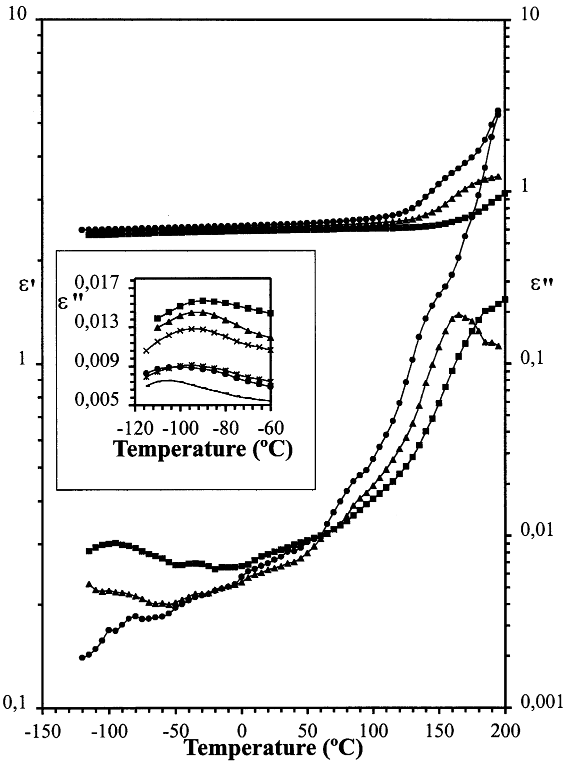


Fig. 1. Main figure: Dielectric permittivity and loss for P2NBM (■) 10^4 Hz, (▲) 10^2 Hz and (●) 1 Hz. Inset showing the low temperature process: (■) 5×10^4 Hz, (▲) 3×10^4 Hz, (×) 2×10^4 Hz, (∗) 10^4 Hz, (●) 5×10^3 Hz and (–) 2×10^3 Hz.

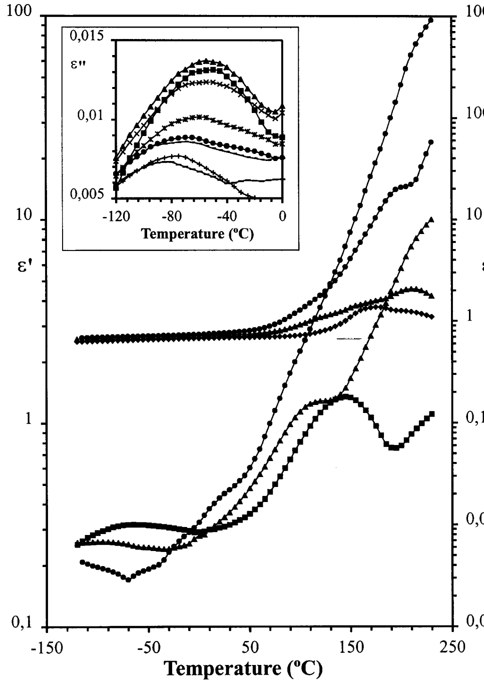


Fig. 2. Main figure: Dielectric permittivity and loss for P3M2NBM (■) 10^4 Hz, (▲) 10^2 Hz and (●) 1 Hz. Inset showing the low temperature process: (■) 5×10^4 Hz, (▲) 3×10^4 Hz, (×) 2×10^4 Hz, (∗) 10^4 Hz, (●) 5×10^3 Hz, (+) 3×10^3 Hz, (–) 2×10^3 Hz and (—) 10^3 Hz.

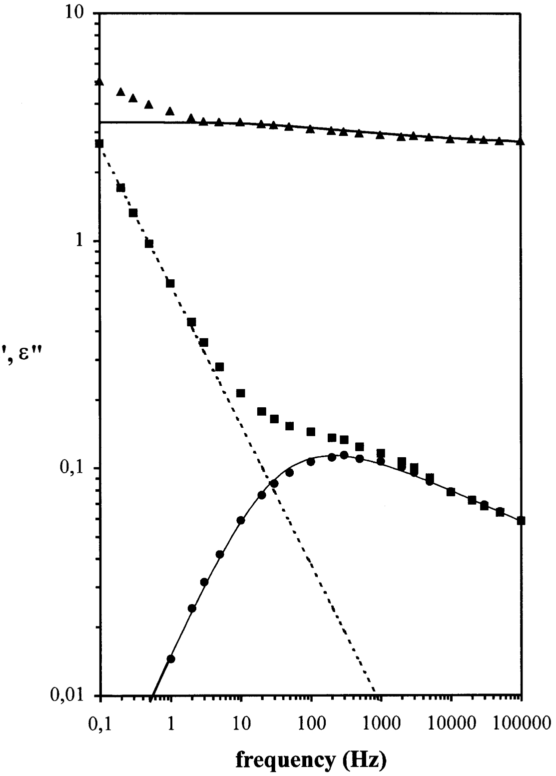


Fig. 3. Dielectric permittivity (▲) and loss (■) for P3M2NBM in the frequency domain at 105°C. The discontinuous straight line represents the conductive effects. Circular black points (●) represent the resulting loss curve after subtraction showing the dipolar α-relaxation. The continuous lines correspond to the Havriliak–Negami curve fit.

Table 1
Parameters of the Havriliak–Negami equation for P2NBM

T (°C)	ϵ_∞	$\Delta\epsilon$	τ (s)	$\bar{\alpha}$	$\bar{\beta}$
165	2.3	1.0	4.0×10^{-3}	0.76	0.21
170	2.2	1.1	1.5×10^{-3}	0.73	0.22
175	2.2	1.2	8.1×10^{-4}	0.69	0.25

Table 2
Parameters of the Havriliak–Negami equation for P3M2NBM

T (°C)	ϵ_∞	$\Delta\epsilon$	τ (s)	$\bar{\alpha}$	$\bar{\beta}$
90	2.59	0.53	1.39×10^{-2}	0.75	0.20
95	2.58	0.60	9.16×10^{-3}	0.69	0.24
100	2.50	0.74	8.39×10^{-3}	0.77	0.17
105	2.41	0.85	6.28×10^{-3}	0.70	0.20

is observed in both polymers. As can be seen, the effect of the methyl substitution in position 3 of the norbornyl group is to decrease the temperature of this relaxational process. At low frequencies, conductive phenomena overlap the loss factor. Owing to the fact that these conductive effects also affects the real part of the complex permittivity, one can conclude that these effects are not only due to free charges conduction but also a blocking electrode process is present. For instance, Fig. 3 shows the loss permittivity of P3M2NBM in the frequency domain at 105°C. At this temperature, secondary processes are absent in the range of the frequencies studied. In order to remove the conductive effects a straight line with slope −1 in a double logarithmic plot $\log\epsilon''$ vs. $\log f$, is used (see Fig. 3). In order to analyse the resulting dipolar α-relaxation, an empirical equation of Havriliak–Negami [15] has been chosen according to which

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{(1+(\mathrm{i}\omega\tau)^{\bar{\alpha}})^{\bar{\beta}}} \tag{1}$$

where $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, and τ, ϵ_0, ϵ_∞ are adjustable parameters.

The regression of the experimental data was obtained by means of the program LEVM6 by MacDonald [16] and the corresponding parameters are given in Tables 1 and 2. The accuracy of this procedure is within 5% of the obtained values.

Moreover, secondary loss peaks are observed in the low temperature side of the experimental curves. The activation energy of these processes has been calculated from the data of the insets in Figs. 1 and 2 by means of an Arrhenius plot (Fig. 4), giving 8.9 and 12.1 kcal/mol for P2NBM and P3M2NBM, respectively. Attempts to fit these absorptions to an empirical Fuoss–Kirkwood equation [17] have been made according to

$$\epsilon'' = \epsilon''_{\max}\,\mathrm{sech}\,\frac{mE_\mathrm{a}}{R}(T^{-1} - T^{-1}_{\max}) \tag{2}$$

In the case of P2NBM, and due to the low strength, it has been not possible to analyse this secondary relaxation in terms of the proceeding equation. The parameters corresponding to P3M2NBM are given in Table 3. These results indicate that the subglass relaxation in P3M2NBM is indeed a broad and weak relaxational process.

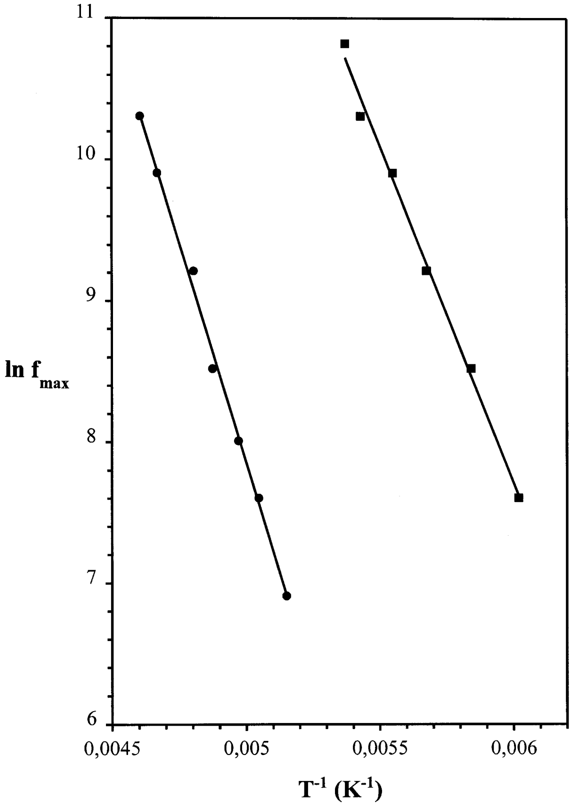


Fig. 4. Arrhenius plot for the secondary relaxations of P2NBM (■) and P3M2NBM (●).

4. Conclusions

As observed in a previous paper [5], the low strength of the observed secondary processes has been attributed to the bulkiness of the side chain. In one case, the low strength of the secondary relaxation prevents the analysis of this peak in terms of an empirical equation. The effect of the methyl substituent on the norbornyl ring is to lower the position of the value of the peak of the α-relaxation about 50 K. Conductive effects are also observed in the low frequency side of the spectra of both polymers.

Table 3
Parameters of Fuoss–Kirkwood equation for β-relaxation of P3M2NBM

f (Hz)	$\epsilon''_{\max}$	$T_{\max}$ (K)	m	$\Delta\epsilon$
20,000	0.012	213	0.10	0.24
10,000	0.010	211	0.09	0.22
5000	0.009	205	0.08	0.22

Acknowledgements

This work was supported by the CICYT through the grant MAT99-1127-C04-03. We express our thanks to FONDECYT, project 8970011 for financial support. C.P. thanks to DIPUC for a Doctoral fellowship. A.G.-B. thanks the Universidad Politécnica de Valencia for a grant.

References

[1] Heijboer J. Molecular basis of transitions and relaxations. In: Meier DJ, editor. Midland macromolecular monographs, vol. 4. London: Gordon & Breach, 1978.
[2] Heijboer J. PhD Thesis. Leiden, The Netherlands; 1972.
[3] Díaz-Calleja R, Saiz E, Riande E, Gargallo L, Radic D. J Polym Sci, Polym Phys Ed 1994;32:1069.
[4] Díaz-Calleja R, Sanchis MJ, Saiz E, Martínez-Piña F, Gargallo G, Radic D, Riande E. J Polym Sci, Polym Phys Ed 2000;38:22179.
[5] Díaz-Calleja R, Martínez-Piña F, Gargallo L, Radic D. Polym Engng Sci 1997;39:882.
[6] Sanchis MJ, Díaz-Calleja R, Gargallo L, Hormazábal A, Radic D. Macromolecules 1999;32:3457.
[7] Díaz-Calleja R, San Román J, Gargallo L, Radic D. Macromol Chem Phys 1998;199:575.
[8] Díaz-Calleja R, García Bernabé A, Sánchez-Martínez E, Hormazábal A, Gargallo L, Radic D. Polymer 2000;41:4811.
[9] Díaz-Calleja R, García-Bernabé A, Hormazábal A, González-Nilo F, Gargallo L, Radic D. Macromolecules, accepted for publication.
[10] Díaz-Calleja R, García-Bernabé A, Hormazábal A, Gargallo L, Radic D. Polymer, submitted for publication.
[11] Gargallo L, Méndez I, Radic D. Makromol Chem 1983;184:1053.
[12] Burtle JG, Turek WN. J Org Chem 1954;19:1567.
[13] Ribes-Greus A, Díaz-Calleja R, Gargallo L, Radic D. Polymer 1989;30:1685.
[14] Sanchis MJ, Díaz-Calleja R, Hormazábal A, Gargallo L, Radic D. Macromolecules 1999;32:3457.
[15] Havriliak S, Negami S. Polymer 1967;8:161.
[16] MacDonald JR. Complex non linear least squares immitance fitting program LEVM6. Department of physics and astronomy, University of North Carolina; 1993.
[17] Fuoss RM, Kirkwood JG. J Am Chem Soc 1941;63:385.