Polymer Bulletin 32, 675–678 (1994)

Polymer Bulletin

Viscoelastic relaxations in poly(dimethylphenyl methacrylates)

Ricardo Díaz Calleja[1,*] **Ligia Gargallo**[2], **and Deodato Radić**[2]

[1]Depto. de Termodinámica Aplicada, E.T.S.I.I., Universidad Politécnica de Valencia,
Apartado 22012, E-46071 Valencia, Spain
[2]Depto. de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile,
Casilla 306, Santiago 22, Chile

Summary

Dynamic mechanical properties of poly(dimethylphenyl methacrylàtes) were studied considering the different positions of the methyl groups on the phenyl ring. In all cases a clear α relaxation can be observed which is associated to the polymer glass transition temperature (Tg). Nevertheless, at lower temperatures, viscoelastic activity is negligible. A correlation between the steric hindrance due to the methyl groups and the temperature at which the relaxation is detected, was established.

Introduction

Viscoeleastic relaxations in polymer are closely related to their structure. It is well known[1] that poly(phenylmethacrylate) (PPhMA) does not show significative viscoelastic activity below Tg. On the other hand, the presence of a -CH_2- spacer group as in the case of poly(benzyl methacrylate) (PBzMA) promotes a larger molecular movility giving rise at least two viscoelastic relaxations but with low intensity[2]. Likewise the glass transition temperature diminishes about 50 °C, relative to that of poly(phenyl methacrylate) (PPhMA). Recent dielectric studies[3] show that besides our observation on PBzMA,[4] poly(phenyl methacrylate) and poly(dimethylphenyl methacrylates)[5] present two slightly dielectric absorptions below Tg. Besides the above considerations relative to secondary relaxations, it is also important to analyze the influence of the substituents in the side group on the glass transition temperature. As it was mentioned above, when the flexibility of the side chain increases the Tg values diminishes. Therefore, it is interesting to study the effect of the side chain structure on the glass transition temperature, for the same substituent but in different positions in the aromatic ring.

In this communication we will analyze the dynamic mechanical relaxation spectra corresponding to four poly(dimethylphenyl methacrylates) (PDMP) where the methyl substitution are located in 2,4; 2,5; 2,6 and 3,5 positions in the aromatic ring, according to the next scheme:

---

[*] Corresponding author

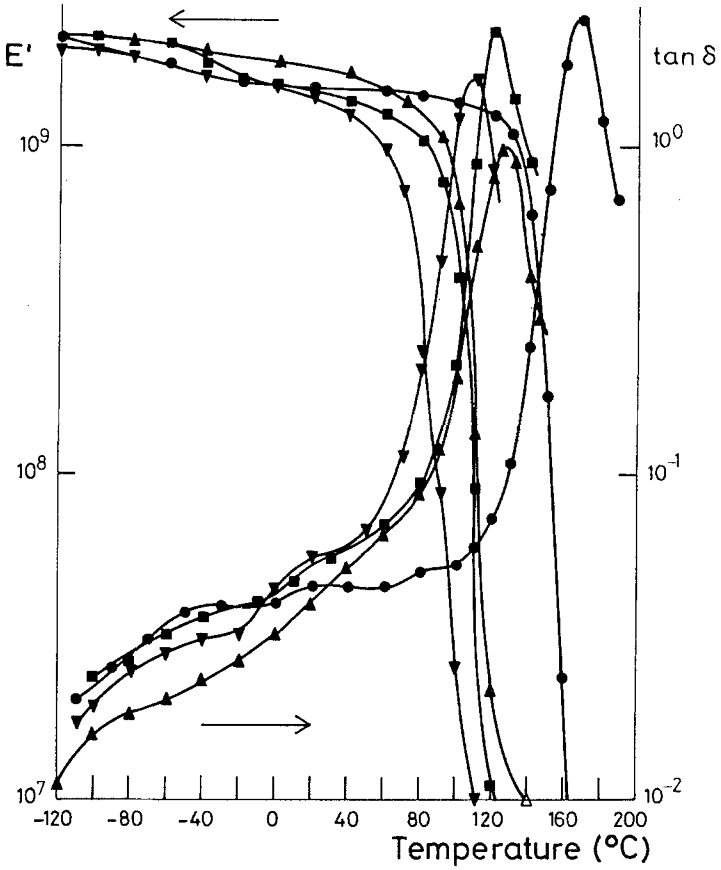
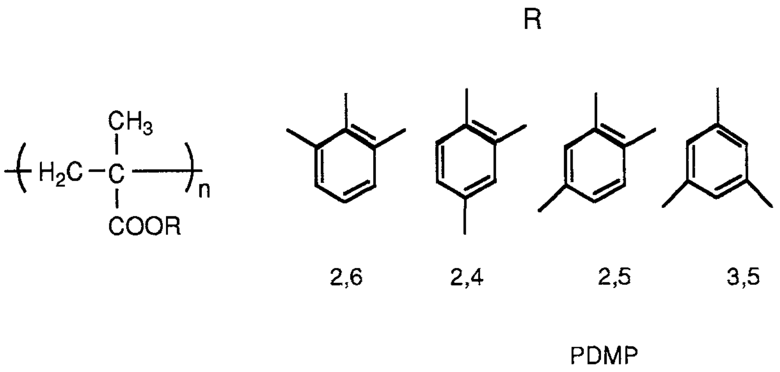


Figure 1. Dependence of storage modulus and loss tangent with temperature for 2,4-PDMP(■), 2,5-PDMP(▼),2,6-PDMP(•) and 3,5-PDMP (Δ)

These results are a consequence of the larger steric hindrance of the di-substitution on 2,6-PDMP relative to the other three polymers. The rotation of the phenyl group is more restricted as a consequence of a lower molecular flexibility, what can be seen through the rigidity factors for these polymers.[6,7]



SCHEME 1

Experimental

Monomer and Polymer Preparation

Monomers were obtained by reaction between methacryloil chloride and the corresponding dimethylphenols, according to methods previously reported.[6,7] Polymerizations of the monomers were carried out in vaccum using α,α'-azobisisobutyronitrile as initiator [2,6,7]

Dynamic mechanical measurements

Samples were obtained by moulding and heating using a dynamic mechanical thermal analyzer DMTA Mark II in flexure single cantilever mode at five frequencies: 0.3; 1.0; 3.0; 10.0 and 30.0 Hz between -120 °C and 20 °C upper than the α relaxation at 1 °C/min.

Results and Discussion

Figure 1 shows the real part of the dynamic modulus and the loss tangent at 1 Hz for all the polymers under study. From this Figure it is possible to observe that 2,6-PDMP is the polymer showing the larger Tg value and 2,5-PDMP the lower, what can be summarized in Table 1.

TABLE 1

Dependence of the temperature of the maximun in tanδ at 1Hz for the α relaxation as function of the position of the methyl substituents for 2,4-PDMP, 2,5-PDMP, 2,6-PDMP and 3,5-PDMP.

Polymer	T °/C
2,4 PDMP	121
2,5 PDMP	108
2,6 PDMP	167
3,5 PDMP	127

Another fact to take into account is that there is no dipole-dipole interaction between both methyl groups due to the antiparalell position of them. For this reason it is possible to think that the glass transition temperature of 2,5-PDMP should be lower because of the higher mobility. These arguments are in good agreement with the results shown in Table 1.

In the vitreous zone there is some viscoelastic activity around -40 °C and 20 °C. Because of the low intensity of these phenomena, it was not possible to calculate the activation energy from the viscoelastic data.

It is interesting to remark that in the case of monosubstituted poly(phenyl acrylate) containing chlorine in the aromatic ring, it has been observed[8] intensive subglass mechanical absorptions which have been attributed to the whole rotation of the side group. As the size of the chlorine group is similar to that of the methyl group, it should be expected the same relaxations in the corresponding monomethyl substituted poly(phenyl acrylates) and also poly(dimethylphenyl) derivatives. On the contrary, in our poly(alkylphenyl methacrylates) the absence of that absorptions should be attributed to the restriction to molecular mobility due to the α-methyl group in poly(methacrylate) chains. In fact, it is very well known[1,8] that the α methyl groups in these systems not only increase considerably the glass transition temperature, but they also reduce the mobility of the groups which would be the responsible of the relaxation associated to the Tg.

It seem clear from our results dealing with poly(benzyl methacrylates)[2] that the absence of methyl substituents on the phenyl ring and the presence of a -CH_2 spacer group increases the molecular mobility, showing two secondary relaxations. Nevertheless they are not enough to compensate the large steric hindrance due to the α-methyl group.

Acknowledgements

This work was supported by GRANT MAT 0695/91 from CICYT. L.G. and D. R. express their thanks to FONDECYT for the financial help.

References

1. HEIJBOER, J. Ph.D. Thesis Leiden, 1972.
2. DIAZ CALLEJA, R., GARGALLO, L. and RADIC', D. Polymer 34, 000 (1993).
3. KIHIRA, Y. and SUGIYAMA, K. Makromol. Chem. 187, 2445 (1986).
4. RIBES-GREUS, A., DIAZ CALLEJA, R., GARGALLO, L. and RADIC', D., Polymer 30, 1685 (1989).
5. DIAZ CALLEJA, R., DEVINE, I., GARGALLO, L. and RADIC', D. Polymer, 34,000 (1993)
6. GARGALLO, L. HAMIDI, N. and RADIC', D. Polymer 31, 924 (1989).
7. GARGALLO, L. HAMIDI, N. and RADIC', D. Polym. Int. 24. 1 (1991).
8. DIAZ CALLEJA, R., RIANDE, E., SAN ROMAN, J. Macromolecules 24, 1854 (1991).

Accepted March 2, 1994 C