Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 1534 – 1538

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[P2.148]

Study of the thermal, dielectric and mechanical properties of poly(methyl methacrylate-co-(1,4,7,10-tetraoxacyclododecan-2-yl)methyl methacrylate) membranes

B. Redondo-Foj*[1], P. Ortiz-Serna[1], M. Carsí[1], M.J. Sanchis[1], R. Díaz-Calleja[1], F. García[2] et al

[1]*Universitat Politècnica de València, Spain,* [2]*Universidad de Burgos, Spain,* [3]*Instituto de Ciencia y Tecnología de Polímeros, Spain*

Background

The 1967 discovery of the selective interaction of metal cations with cyclic oxyethylene sequences was the begin of the host-guest chemistry, the cornerstone of supramolecular chemistry[1,2]. The term crown ether was defined to describe the ability of the oxyethylene cyclic molecules to crown cations. The interaction of the ether groups with cations by ion-dipole interactions is especially favored in the crown ethers. This is due to the fact that a favorable conformation is imposed by the alicyclic structure. The ability of crown ethers to interact selectively with cations opens new possibilities in technological applications; such as ion selective electrodes, the development of liquid or supported liquid membrane, the design of extraction systems for purification, recovery or decontamination, and the production of catalysts for organic or inorganic reactions [3].

However, the crown ethers have limitations in technological applications, since they are low molecular weight compounds. They are soluble in most solvents so their use in separation and reuse is complicated. Moreover, they possess low thermal and chemical stability. Therefore, a physical support is required for most applications so they are immobilized and their migration is reduced.

The preparation of polymers with crown ethers extends the possibilities of new technological applications related to sensors, actuators [4, 5] permselective membranes, [6] catalysis, [7] etc. Hence, some research work has been focused on the use of this type of polymers, especially for species separation, a problem of great industrial interest [8–13].

One of the aims of this work was study the effect of the small variations in the chemical structure in the properties of the membranes. This type of analysis can provide key information for the development of new membranes based on polymers with specific properties. The membranes must show high local and/or segmental mobility at the working temperature (generally around ambient temperature), together with dimensional stability. In this sense, the study of crown ethers anchored to the structure of a polymer is very interesting. To accomplish the objective, two membranes of poly(methyl methacrylate-co-(1,4,7,10-tetraoxacyclododecan-2-yl) methyl methacrylate) (10/90 and 25/75) has been synthesized and analyzed by using Differential Scanning Calorimetry (DSC), dynamic mechanical analysis (DMA) and Broadband Dielectric Spectroscopy (BDS)[14-16]. Unfortunately, the response of polymers to perturbation fields can only be obtained in a few decades of time/frequency in the case of mechanical force fields so that obtaining information over a long frequency/time range requires the application of the temperature-frequency/time superposition principle, which only holds for thermorheological simple systems. This disadvantage can be overcome using broadband dielectric spectroscopy (BDS), a technique that enables analysis of the chains response over more than 10 decades in the frequency domain.

doi:10.1016/j.proeng.2012.08.856

Methods

The two copolymers will be called hereafter CR4MA X/Y where X stand for the molar fraction of (1,4,7,10-tetraoxacyclododecan-2-yl)methyl methacrylate (CR4MA) and Y stands for the molar fraction of methyl methacrylate (MMA). The structures of monomers appear in Figure 1. The monomer (1,4,7,10-tetraoxacyclododecan-2-yl) methyl methacrylate (CR4MA) was prepared following a specific synthetic route.[17]

The glass transition temperatures of CR4MA 10/90 and CR4MA 25/75 membranes were measured with a DSC-Q20 from TA Instruments at a heating rate of 10K/min. The gas used in the measurement, in order to obtain an inert atmosphere, was N_2.

Dynamic mechanical thermal analyzer DMA-Q800 TA-Instruments was used for the evaluation of the complex modulus (E^*) and mechanical loss factor (tan δ). The temperature range over which properties was measured from 143 to 453K at a heating rate of 3 K/min. The tests were carried out at different frequencies 0.3, 1, 3, 10 and 30 Hz in a tension mode.

BDS analysis was performed on a Novocontrol Broadband Dielectric Spectrometer System. The isothermal measurements were carried out from frequencies between 10^{-1} to 10^6 Hz and from 133 to 453K in 5K intervals, on disc-shaped films of about 80 μm thickness and 20 mm diameter.

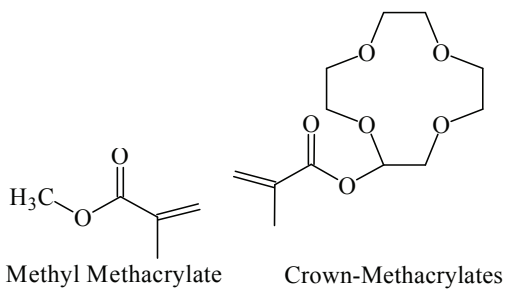

Figure 1. Monomers used to synthesize CR4MA10/90 and CR4MA 25/75.

Results

Glass transition temperature evaluated from DSC spectra was taken as the intersection of the base line of the glassy region with the tangent to the endotherm in the middle point. The values of T_g for CR4MA 10/90 and CR4MA 25/75 membranes are 382.28K and 365.81K respectively.

Figure 2 shows the storage and loss modulus of MMA/CR4MA (90/10) membrane at five frequencies (0.3, 1, 3, 10 and 30 Hz) in the temperature range studied. This Figure clearly shows the existence of four relaxations. In the isochrone of 1 Hz, we can observe an α-relaxation process, which is associated with the glass transition temperature, at ~413 K. At lower temperature, three secondary relaxations associated with local movements of side chain can be observed. The β-relaxation process centered at ~283K appears intimately overlapped with the γ-relaxation centered at ~273K and finally, δ-relaxation emerges near 153K. For MMA/CR4MA (25/75) membrane, a similar mechanical behaviour was obtained.

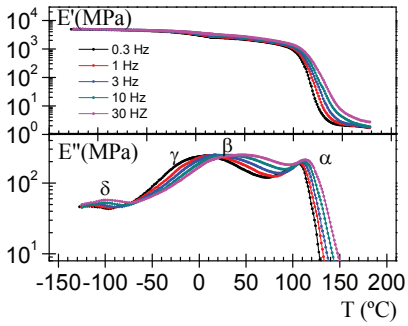

Figure 2. Storage and loss modulus as a function of the temperature at 0.3, 1, 3, 10 and 30 Hz for CR4MA 10/90.

By comparing Vogel-Fulcher-Tammann-Hesse (VFTH) [18] equation with the Doolittle expression [19] and by using the Arrhenius plot, the fraction of free volume at the glass transition temperature and the free volume expansion coefficient $\alpha_f = (1/V)(\partial V/\partial T)_p$ are estimated. The values obtained for both membranes are near to 0.025 and $4 \cdot 10^{-4} K^{-1}$, respectively.

Owing to the high contributions of the conductivity processes to the dielectric loss, the frequency at the peak maximum for α-relaxation cannot be detected in the dielectric spectra. However, pure ohmic conduction can be removed if ε'' is obtained from ε' using Kramers-Kroning equation [15]. As an example, in Figure 3 the loss permittivity as a function of the temperature are plotted at several frequencies for CR4MA 10/90 membrane.

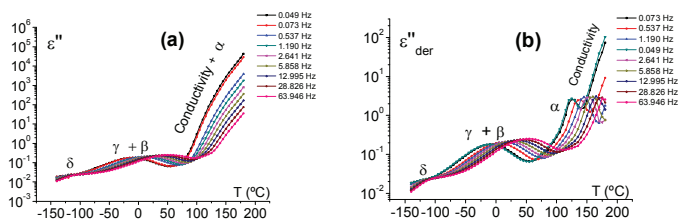

Figure 3. The loss permittivity as a function of temperature for CR4MA 10/90 at several frequencies (a) before and (b) after having removed the conductivity.

The spectrum obtained for CR4MA 25/75 membrane is similar to that one obtained for the CR4MA 10/90 membrane. From our analysis results, it is observed that the strength of the secondary processes is higher for the membrane with lower crown-ether content. This fact can be related with the steric effects imposed by the crown units.

Acknowledgements

This work was financially supported by the DGCYT and CAM through the Grant MAT2008-06725-C03.

References

[1] C. J Pedersen, Cyclic Polyethers and Their Complexes with Metal Salts, *Journal of the American Chemical Society* 89(26) (1967) 7017–7036.

[2] C. J.Pedersen, Cyclic Polyethers and Their Complexes with Metal Salts, *Journal of the American Chemical Society* 89(10) (1967) 2495–2496.

[3] C. J. Pedersen, The discovery of crown ethers. Nobel lecture 1987; 8.

[4] P.L. Drake, G.J. Price, Crown-ether containing copolymers as selective membranes for quartz crystal microbalance chemical sensors, *Polymer International* 49 (2000) 926-930.

[5] S. Shinkai, M. Takeuchi, A. Ikeda, in Polymer Sensors and Actuators, Y. Osada,; D.E. De Rossi, , Ed.; Springer: Berlin, 2000; Cp. 6

[6] T. Sata, T. Sata, W. Yang, Studies on cation-exchange membranes having permselectivity between cations in electrodialysis *Journal of Membrane Science* 206 (1-2) (2002) 31-60.

[7] H. Watanabe, Y. Iijima, W. Fukuda, M. Tomoi, Synthesis and phase-transfer catalytic activity of novel chiral crown ethers immobilized onto polystyrene supports *Reactive& Functional Polymer* 37(1-3) (1998) 101.

[8] S. Habaue, M. Morita, Y. Okamoto, Anionic Polymerization of Macrocyclic α-(Alkoxymethyl)acrylates Leading to Novel Vinyl Polymer with Crown Ether Type Side

Chain, *Macromolecules* 35 (2002) 2432–2434.

[9] X-S. Feng, L-F. Yan, J. Wen, C-Y. Pan , Synthesis and self-assembly study of two-armed polymers containing crown ether core, *Polymer* 43(10) (2002) 3131-3137.

[10] V. Percec, R. Randall, Liquid crystal polymers containing macroheterocyclic ligands. 2. Side chain liquid crystal polysiloxanes and polymethacrylates containing 4-(ω -alkan-1-yloxy)-4'-(4'-carboxybenzo-15-crown-5)biphenyl side groups, *Macromolecules* 22 (1989) 4408–4412.

[11] M.F.M. Roks, R.J.M. Nolte, Biomimetic macromolecular chemistry: design and synthesis of an artificial ion channel based on a polymer containing cofacially stacked crown ether rings. Incorporation in dihexadecyl phosphate vesicles and study of cobalt ion transport, *Macromolecules* 25 (1992) 5398–5407.

[12] V.P. Privalko, E.S. Khaenko, A.P. Grekov, Yu. Savelyev, Structure-property relationships for a series of crown ether-containing polyurethane-ureas, *Polymer* 35 (1994) 1730–1738.

[13] P. Tiemblo, J. Guzmán, E. Riande, F. García, J.M. García, Gas transport properties of crown-ether methacrylic polymers: poly(1,4,7,10-tetraoxacyclododecan-2-yl) methyl methacrylate, *Polymer* 44 (2003) 6773-6780.

[14] N.G. McCrum, B.E. Read, G.Williams, Anelastic, Dielectric Effects in Polymeric Solids. London: Wiley 1967.

[15] F. Kremer, A. Schönhals,; *Broadband Dielectric Spectroscopy,* Springer-Verlag Berlin Heidelberg, 2003.

[16] E.Riande, R. Díaz-Calleja, , Electrical Properties of Polymers; Dekker: New York, 2004

[17] F. García, J.M. García, F. Rubio, P. Tiemblo, J. Guzmán, E. Riande, Synthesis and radical polymerization of methacrylic monomers with crown ethers in the ester residue: 1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate, *Polymer* 44 (2003) 6773–6780.

[18] H. Vogel Temperature dependence of viscosity of melts, *Physik. Z.* 22 (1921) 645–646; G.S. Fulcher Analysis of recent measurements of the viscosity of glasses, *Journal of American*

Ceramic Society 8 (1925) 339–355; G. Tamman, W. Hesse The dependence of the viscosity on temperature for super-cooled liquids*, Zeitschrift für anorganische und allgemeine Chemie* 156 (1926) 245–257.

[19] A.K. Doolittle, Studies in Newtonian Flow. II. The Dependence of the Viscosity of Liquids on Free-Space, *Journal of Applied Physic* 22(12) (1951) 1471-1475; A.K. Doolittle Studies in Newtonian Flow. III. The Dependence of the Viscosity of Liquids on Molecular Weight and Free Space (in Homologous Series), *Journal of Applied Physic* 23(2) (1952) 236-243

Keywords: Crown ether, Mehacrylates, relaxations, conductivity