Polymer Bulletin 36, 617–621 (1996)

Polymer Bulletin

The effect of crosslinking on the glass transition temperature and the density of diethylene glycol bis(allylcarbonate) polymer networks

J. Stejny

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue,
Bristol BS8 1TL, UK

Received: 1 December 1995/Accepted: 7 February 1996

Summary.

The effect of crosslinking on the glass transition temperature and the specific volume of poly(diethylene glycol bis(allyl carbonate)) networks was studied using a series of networks with progressively decreasing density of crosslinks. The networks were prepared by a bulk copolymerisation of ethylene glycol bis(allyl carbonate) with an increasing amount of allyl ethoxyethyl carbonate. It was found that their glass transition temperature determined by the Dynamic Mechanical Thermal Analysis decreases linearly with increasing concentration of the monoallyl comonomer whilst the increase in their specific volume is non-linear. This is explained by the non-equilibrium state of the networks at the temperature of the specific volume measurement.

Introduction.

Poly(diethylene glycol bis(allyl carbonate)) commercially known as CR-39 resin is a network polymer widely used as a glass substitute for applications in optics (1). Apart from its good optical properties it has a unique sensitivity to particle radiation which is used in its current application as a nuclear particle track detector (2). The combination of its high radiation sensitivity and good optical properties offers a good prospect for its potential application as ion beam induced optical waveguides and gradient refractive index materials (3).

The resin is made by a free radical polymerisation of liquid monomer in bulk. The polymerisation is initiated by peroxides, the allyl groups of the diallyl monomer polymerise independently and are included into different chains. This results in a formation of a three dimensional network consisting of short polyallyl chains connected by diethylene glycol dicarbonate links.

Previous work has shown (4) that the glass transition temperature, defined as the temperature of the loss tangent peak maximum, depends on the concentration of the initiator. The highest glass transition temperature is obtained when the concentration of the initiator is just sufficient to polymerise all allyl groups which are capable to polymerise at the temperature of curing. The decrease of the T_g at initiator concentrations higher than this optimum is explained by the decrease of the polyallyl chain lengths with the increasing concentration of the initiator. This reduces the overall density of crosslinks of the resin together with its glass transition temperature when all available allyl groups are polymerised. It was concluded (4) that the density of crosslinks in CR-39 networks is determined by two parameters namely the concentration of unpolymerised allyl groups and the length of polyallyl chains. Both are dependent on the concentration of the initiator and on the polymerisation conditions.

In order to eliminate the effect of polyallyl chain length on the glass transition temperature of partly polymerised CR-39, model networks were prepared by copolymerising diethylene glycol bis(allyl carbonate) with allyl ethoxyethyl carbonate. The chemical structure of the comonomer was chosen to be as close as possible to the CR-39 monomer so that the reactivity of the allyl groups is similar in both comonomers hence the copolymerisation is expected to be random. The similarity of the comonomers also reduces the copolymer effect on the glass transition temperature therefore its change is mainly caused by crosslinking. The copolymerisations were carried in bulk using the same initiator concentration and the same polymerisation conditions in order to keep the polyallyl chain length constant. The initiator concentration and the curing conditions used were chosen to enable the polymerisation to reach maximum conversion hence the density of crosslinks of the network was controlled by the amount of the monoallyl comonomer.

Experimental.

Materials.

Allyl ethoxyethyl carbonate CH_2=CH-CH_2-0C00-CH_2-CH_2-0-CH_2-CH_3 was prepared from allyl chlorocarbonate and ethoxyethanol according to the reaction:

$$CH_2\text{=CH-}CH_2\text{-0COCl + H0-}CH_2\text{-}CH_2\text{-0-}CH_2\text{-}CH_3 \xrightarrow{\text{pyridine}}$$
$$CH_2\text{=CH-}CH_2\text{-0C00-}CH_2\text{-}CH_2\text{-0-}CH_2\text{-}CH_3\text{ + HCl}$$

The reaction products were extracted several times with water and dichloromethane, the dichloromethane fraction was collected, dichloromethane evaporated and the product purified by vacuum distillation.

Diethylene glycol bis(allyl carbonate) (CH_2=CH-CH_2-0C00-CH_2-CH_2-$)_2$0, CR-39 monomer - was obtained from AKZO Chemie under the trade name Nouryset and was used without purification.

The initiator was tert-butyl peroxide obtained from Aldrich Chemical Comp.

Polymerisation.

Mixtures of CR-39 monomer with different amounts of monoallyl comonomer and containing 1% of tert-butyl peroxide were polymerised between glass plates separated with a 1mm spacer in a thermostat controlled by a temperature programmer. The curing regime found suitable for CR-39 polymerisation with tert-butyl peroxide was used (4). No allyl groups were found in the copolymers by Raman spectroscopy (4) confirming that full conversion was achieved.

Density measurement.

The density of the polymers at 25^{o}C was determined by a flotation method using solutions of calcium chloride in water as the flotation medium.

Determination of the glass transition temperature.

A Rheometrics RMS 800 dynamic mechanical spectrometer was employed to obtain the dependence of the storage and loss moduli and the loss tangent on temperature at the frequency of 1 rad/s. The temperature of the maximum in the loss tangent peak was taken as the glass transition temperature. A typical loss tangent peak is shown in Fig.1.

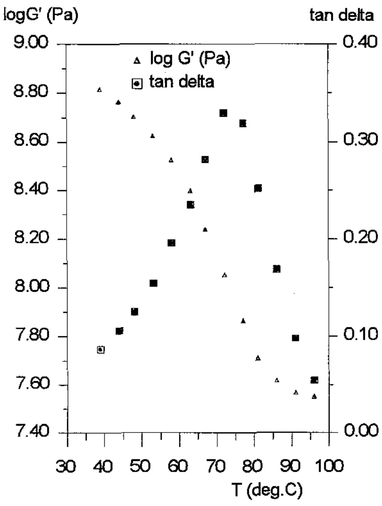

Fig. 1.
Dependence of the storage modulus G' and the loss tangent on temperature.

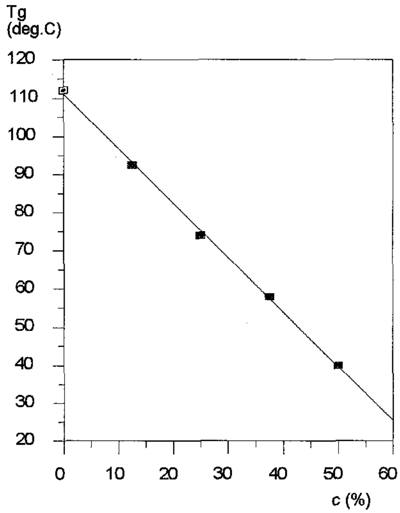

Fig. 2.
Dependence of the glass transition temperature T_g on the weight concentration of the monoallyl comonomer.

Results and Discussion.

The dependence of the glass transition temperature determined by DMTA on the concentration of the monoallyl comonomer is plotted in Fig. 2. The plot shows that the glass transition temperature decreases linearly from its maximum value of 112°C for the pure CR-39 to the value of 40°C for the copolymer containing 50% by weight of the monoallyl comonomer. The least square fitting gives the equation:
T_g (deg.C.) = 111 - 1.428 c (%) with the correlation coefficient $r^2 = 0.9989$ confirming a very good fit.

A characteristic feature of diallyl networks studied in this work is that they are made by a chain-growth copolymerisation of diunsaturated with monounsaturated monomers. According to the classification of polymer networks introduced by Schefer and Gottlieb (5) such polymers belong to the class 3 networks where the typical representatives of this class are divinylbenzene - styrene and diacrylate - monoacrylate copolymers. The density of crosslinks in such systems depends on the concentration of the diunsaturated comonomer and the conversion, it is usually expressed in moles of crosslinks/gram and for full conversion it is equal to w_d/M_d, where w_d is the weight fraction of the diunsaturated comonomer and M_d is its molecular weight. The effect of the density of crosslinks on the glass transition temperature of these copolymers was studied by Ueberreiter and Kanig (6) and Loshaek (7) who found that the dependence of T_g on the density of crosslinks is approximately linear. This is in agreement with theoretical treatments of this problem (8-10) which predict a linear dependence of the T_g in the low to intermediate region of crosslink density for this class of networks. The fact that our results give better linear fit can be explained by the lower range of crosslink densities accessible for CR-39 copolymers where the link between the double bonds in the diallyl is considerably longer than in the diacrylate monomer or in the divinyl benzene studied in the past (6,7). Also, it seems likely that the glass transition temperature measured as the position of the maximum of the loss tangent peak can be read more accurately than the T_g measured by the specific volume or the specific heat methods.

The linear dependence of the glass transition temperature on the concentration of the monoallyl comonomer is in agreement with the assumption that the average length of polyallyl chains is not affected by the copolymer composition. It is also compatible with the explanation of the maximum in the T_g dependence of the CR-39 homopolymer on the concentration of the initiator observed previously(4). The GPC analysis of the polyallyl chains in the homopolymer demonstrated that the average chain length was short and decreased steadily with the increasing concentration of the initiator(11). It was shown that the conversion of allyl groups increased with the initiator resulting in the increase of the T_g, however this effect was reduced by the decrease in the polyallyl chain length. At high initiator concentrations, where the increase in the conversion with the initiator concentration was small, the reduction in the T_g due to the chain shortening became dominant and the T_g started decreasing regardless of the small increase in the conversion. These opposing effects explained not only the appearance of the maximum in the dependence of the T_g on the initiator concentration observed by Ahmad and Stejny (4) but they were also suggested to be responsible for the maximum observed in the dependence of the density and the refractive index on the initiator concentration (12). A contribution to the decrease in the T_g dependence can be expected if the decomposition of the initiator leaves low molecular weight fragments in the polymer which can act as a plasticiser.

Fig.3. shows the results of the density measurements as the dependence of the specific volume of the copolymers on the concentration of the monoallyl comonomer. The experimental points fit a parabolic curve $V_{sp}(\text{ml/g}) = 9.1048\text{x}10^{-6}\ c^2 + 3.2286\text{x}10^{-5}\ c + 0.76635$ with the correlation coefficient $r^2 = 0.99954$. The densities were measured at 25°C which is below the glass transition temperature of all but two samples. The structure of polymers is metastable below their glass transition temperatures and the values of the specific volume obtained below T_g are higher than those which correspond to the thermodynamic equilibrium. The difference between the measured specific volume and its equilibrium value increases with the difference between the T_g and the temperature of the measurement.

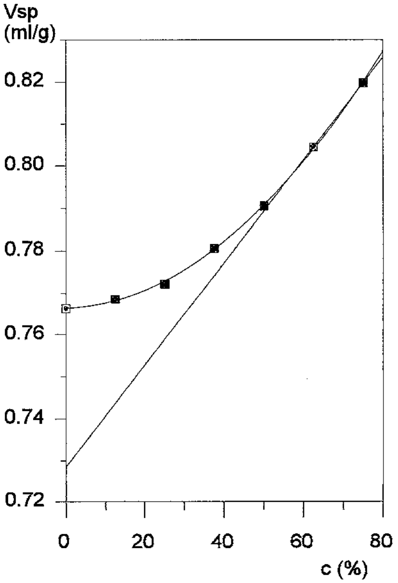

Fig.3.
Dependence of the specific volume Vsp on the weight concentration of the mono allyl comonomer.

Equilibrium specific volume at temperatures below the glass transition are estimated by using the linear part of the temperature dependence of the specific volume at temperatures above the T_g and extrapolating it to the temperatures below the glass transition. If the temperature dependence of the specific volume above and below the T_g is approximated by straight lines with the specific thermal expansivity coefficients e_l and e_g, the difference between the measured and the equilibrium values of the specific volume can be calculated using the equation: $V - V_{eq} = (e_l - e_g)(T_g - T)$ (eq.1.) where V is the specific volume measured at the temperature T and V_{eq} is the equilibrium specific volume at the same temperature. However, this approximation is not valid for the temperature region close to the glass transition where the specific volume dependence is non-linear.

If the contribution of chemical groups to the volume of CR-39 copolymer networks is additive then the dependence of the equilibrium specific volume on the weight fraction of the monoallyl component should be linear. Figure 3 shows a linear extrapolation of the specific volume dependence using the values obtained on the samples which are in the rubbery state at 25°C. This line should represent the dependence of the equilibrium specific volume on the network composition providing that the contribution of comonomers is additive. The value of the equilibrium specific volume obtained by this way for pure CR-39 homopolymer is 0.7285 ml/g which is 0.0378 ml/g lower than the metastable value actually measured. Substituting this difference into the eq.1. the value of 4.34×10^{-4} ml/g K is obtained for the difference in the specific expansivity coefficients e_l-e_g which is well within the range obtained for this parameter in many amorphous polymers (13). This suggests that the dependence of the equilibrium specific volume on the composition of the CR-39 copolymer, hence on its crosslink density, could be linear. However, a direct measurement of the equilibrium specific volume on the crosslink density is required to confirm this suggestion.

References.

1. Schildknecht CE (1986) Diallyl and related polymers. In: Mark HF,Bikales NM, Overberger CG, Menges G (eds) Encyclopedia of Polymer Science and Engineering. Wiley-Interscience, NewYork, vol. 4. pp. 779-811
2. Henshaw DL, Griffiths N, Landen OAL, Benton EV (1981) Nucl. Instr. and Meth. 180: 65
3. Bennamane B, Decossas JL, Gagnadre C, Vareille JC (1991) Nucl. Instr. and Meth. B 62: 103
4. Ahmad S, Stejny J (1991) Nucl. Tracks Radiat. Meas. 19: 11
5. Schefer A, Gottlieb M (1992) Macromolecules 25: 4036
6. Ueberreiter K, Kanig G (1950) J. Chem. Phys. 18: 399
7. Loshaek S (1955) J. Polymer Sci. 15: 391
8. Fox TG, Loshaek S (1955) J. Polymer Sci. 15: 371
9. Reekmans BJ, Shi Ji-Feng, Pyati M, MacKnight WJ, Lillya CP (1995) Acta Polymer. 46: 12
10. Stutz H, Illers KH, Mertes J (1990) J. Polymer Sci. B 28: 1483
11. Stejny J, Portwood T (1986) Nucl. Tracks 12: 121
12. Darraud C, Bennamane B, Gagnadre C, Decossas JL, Vareille JC, Stejny J (1994) Appl. Optics 33: 3338
13. Van Krevelen DW (1976) Properties of polymers. Elsevier, Amsterdam Oxford New York