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Properties of Partially Cured Networks. 2. The Glass Transition

Claudius Feger and William J. MacKnight*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received March 5, 1984*

ABSTRACT: The increase of the glass transition temperature during the isothermal cure of a model network formed by the reaction of α,ω-dihydroxypoly(propylene oxide) with tris(4-isocyanatophenyl) thiophosphate has been investigated. It is shown that the reaction proceeds first under kinetic control and then under diffusion control upon which is superimposed an intramolecular reaction beyond the gel point. Loop formation occurring during the intramolecular reaction leads to a decrease in the rate of the T_g increase due to plasticization. The dependence of the T_g change on the degree of cure is treated by a WLF approach. The diffusion-controlled part of the cure of the model network investigated and also that of two epoxy resins follow a master curve. Broadening of the glass transition in the model network is attributed to the influence of increasing hydrogen bonding between urethane NH and ether oxygen groups.

Introduction

The measurement of T_g during an isothermal cure is often a difficult task. This is due to the fact that at low temperatures curing systems often vitrify at low conversion and then the reaction is more or less stopped.[1] On the other hand, at high curing temperature reactions are often so fast that T_g measurements are not possible during the cure. However, T_g change accompanying the cure of such systems has been measured by reacting the systems at different temperatures and determining the conversion at which vitrification occurs.[2-4] The T_g increase during isothermal cure cannot be investigated in that way and the method works only if the curing reaction really is stopped by the vitrification.

The investigation of processes occurring during isothermal cure over the whole range of conversion is possible with certain systems.[5] These systems must cure slowly even at temperatures above the final network T_g. With a knowledge of the curing kinetics the T_g increase with degree of reaction can be correlated with conversion.

In our previous paper[6] we described the kinetics of a slowly curing model network-forming system. The use of model networks in investigations of partially cured systems is desirable because of the ease with which their well-defined structures can be related to their properties. This will be demonstrated in the present work.

Experimental Section

Materials. The system is the same which has been used in our previous work.[6] It consists of α,ω-dihydroxypoly(propylene oxide) with molecular weight 1000 (PPO1000) obtained from Aldrich Chemical Co. and tris(isocyanatophenyl) thiophosphate (triisocyanate) obtained from Mobay Corp.

Analytical data have been given elsewhere as well as methods for purification of prepolymer and cross-link agent and the synthetic procedure for the network formation.[6]

Calorimetry and Sample Preparation. All glass transition temperatures and the incremental change in heat capacity at T_g were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, DSC-2. Heating rate was 20 °C/min. The samples used have been prepared by transferring a drop (about 7–10 mg) of the clear curing mixture to a Perkin-Elmer aluminum sample pan for liquid samples. The sample was kept at −80 °C for about 15 min before being placed in the DSC. Once there, it was not removed until the end of the cure.

The T_g was measured after the sample was cooled at the fastest rate to between 180 (in the early stages of cure) and 210 K where it was allowed to remain for 10–15 min. Each measurement was repeated four or five times. After the measurements, the sample was heated to the curing temperature, 303 K, within ~30 s. Measurement of the width of the glass transition represents an average of 4–5 determinations and is defined as the temperature interval between the intersection of the line drawn through the inflection of the heat capacity change at the transition with the lines drawn through the extrapolated base lines before and after the transition.

Results and Discussion

Change in $\Delta C_p(T_g)$ and Width of the Glass Transition. Figure 1 shows T_g vs. time for the cure of PPO1000–triisocyanate at 303 K. Figure 2 shows some of the corresponding DSC traces.

Two features are easily observed. First, $\Delta C_p(T_g)$ decreases with increasing T_g and, second, the glass transition becomes broader as cure proceeds. A decrease in $\Delta C_p(T_g)$ with increasing T_g is expected due to different slopes for C_p(glass) and C_p(rubber).[5]

Broadening of the glass transition with increasing cross-link density has been observed in divinylbenzene cross-linked polystyrene prepared by radical copolymerization.[7] This has been attributed to a broadening of the molecular weight distribution of the chains between cross-link points. However, in network formation proceeding through end-linking reactions the distribution of molecular weights between cross-links is determined by the prepolymer molecular weight distribution and does not change. Data of the diglycidyl ether of bisphenol A type prepolymers cured with phthalic anhydride show no glass transition broadening with increasing cross-link density.[5] The explanation for the behavior observed here becomes obvious when the data are plotted against conversion (Figure 3). Up to very high conversions a linear relationship is found ($\Delta T = 0.112(\text{conversion }(\%)) + 5.4$). The only quantity increasing linearly with conversion is the concentration of urethane groups, i.e., of NH groups. As has been shown,[8] the urethane NH group forms hydrogen

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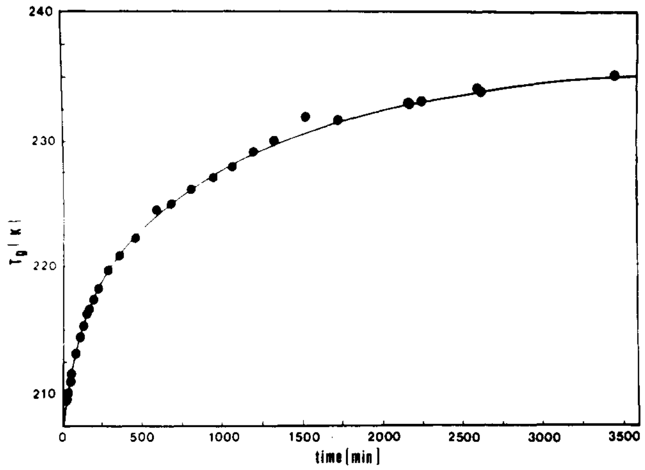

Figure 1. T_g vs. time for cure of PPO1000–triisocyanate at 303 K.

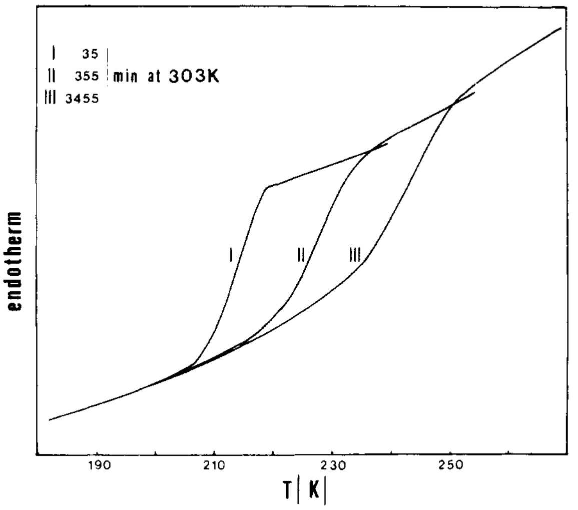

Figure 2. Effect of cure on the glass transition of PPO1000–triisocyanate at 303 K. C_p in arbitrary units.

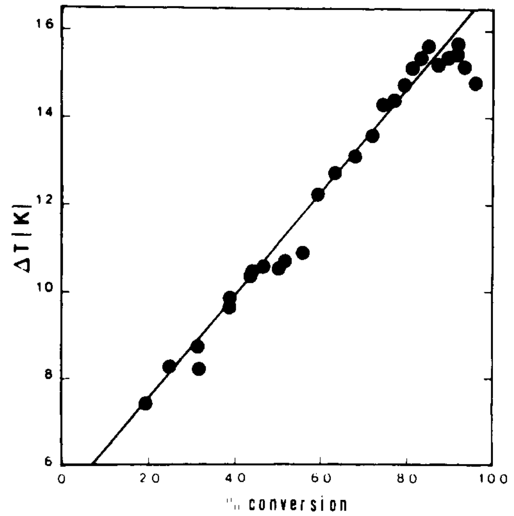

Figure 3. Width of glass transition ΔT (°C) vs. conversion for cure of PPO1000–triisocyanate at 303 K.

bonds to the PPO ether oxygen, slowing down the movement of the PPO chains. Through the hydrogen bonds the segment length becomes statistically distributed—hence the broadening of the glass transition. This explanation is supported by the fact that a PPO1000–TDI copolymer shows greater broadening of the glass transition (ΔT = 8 K) compared to PPO1000 prepolymer (ΔT = 3.5 K).

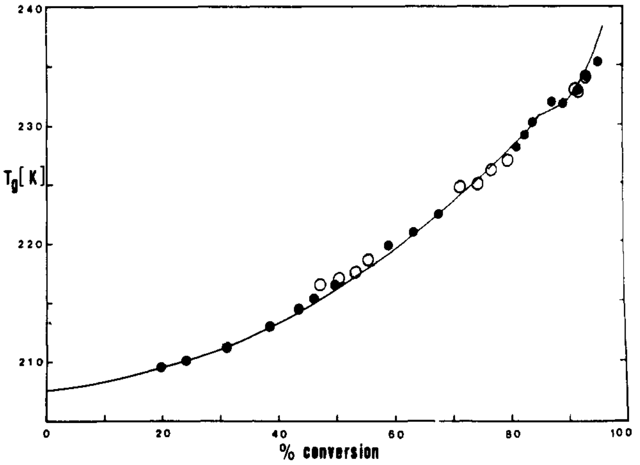

Figure 4. T_g vs. conversion for cure of PPO1000–triisocyanate at 303 K. Results of two experiments are given (filled and unfilled circles). Note the good agreement.

However, as comparison of the copolymer data with the network show, the absolute values for the width of the glass transition depend not only on the NH concentration but also on the structure of the urethane. Nevertheless, within one class of urethanes the broadening should depend only on the NH concentration.

At high conversion (around the gel point) the extent of broadening of the transition seems to stabilize or even to decrease (Figure 3). This is probably due to steric restrictions imposed on the cross-link points at the higher cross-link densities.

Dependence of T_g on Conversion and Time. In DSC experiments long-chain segments are activated at lower temperature than short ones.[7] The longest chain segments in the network considered are the non-hydrogen-bonded PPO chains with molecular weight 1000. Measuring the onset of the glass transition with conversion should therefore give the increase of T_g for the free non-hydrogen-bonded chain. The change in T_g should then reflect only the effect of copolymerization and cross-linking.[9] The experimental values for this system are plotted in Figure 4.

DiBenedetto, as cited by Nielson,[9] proposed an equation relating the change of T_g during cure to conversion. Assuming that the ratio between the lattice energies for cross-linked and un-cross-linked polymer $\epsilon_x/\epsilon_m \sim 1$, DiBenedetto's equation is given by

$$T_{g,0}/T_g = 1 - (F_x/F_m - 1)p \qquad (1)$$

where $T_{g,0}$ is the glass transition temperature at zero conversion, F_x/F_m is the ratio between the mobilities for cross-linked and un-cross-linked segments, and p is the conversion at which the glass transition temperature is T_g. Although F_x/F_m was expected to be zero, values of $0 < F_x/F_m < 1$ were found experimentally. For similar polymers at the same conversion, the ratio is higher the lower the cross-link density.[10] To apply eq 1 $T_{g,0}$ has to be known. This can be approximately calculated by using the Fox equation[11]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

with $w_{1,2}$ and $T_{g1,2}$ the weight fraction and the T_g of component 1 and 2, respectively. The value obtained for $T_{g,0}$ is 209.3 K (with T_g(PPO1000) = 200 K and T_g(triisocyanate) = 244 K). This value is in good agreement with the extrapolated value 207.5 K, which gives best fits between experiment and eq 1 as well as eq 3 (Figure 4).

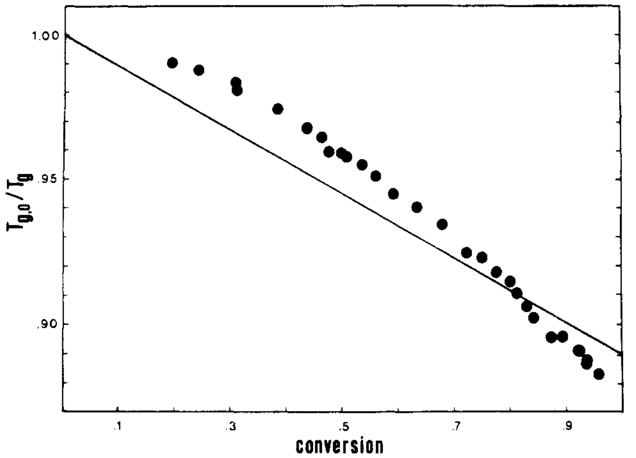

Figure 5. Comparison of DiBenedetto's equation (eq 1) with experiment using $F_x/F_m = 0.89$.

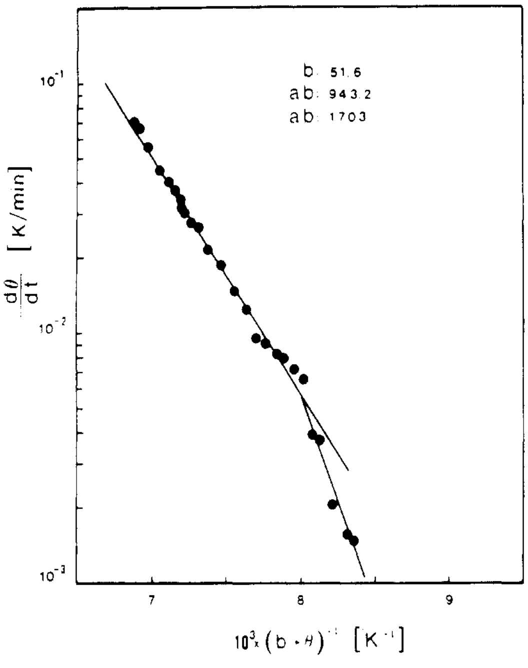

Figure 6. log ($-$dΘ/dt) vs. $(b + \Theta)^{-1}$ for cure of PPO1000–triisocyanate at 303 K. The two lines are best fits through the experimental points. Slopes are 943.2 and 1703, respectively.

According to eq 1, plotting $T_{g,0}/T_g$ vs. conversion, p (Figure 5), should result in a straight line with slope $F_x/F_m - 1$ and intercept 1. The best least-squares fit with eq 1 is obtained with $F_x/F_m = 0.89$. This indicates high mobility of the three functional cross-link points.[10] This is reasonable due to the low functionality and the ether groups of the cross-linking agent.

Although eq 1 describes the data qualitatively, the experimental values deviate significantly from a straight line (see also ref 10). We, therefore, tried another approach to analyze our data. Gordon and Simpson[12] described aging phenomena in thermosets using the WLF concept. Accordingly, the time dependence of the T_g is given by

$$\log (\mathrm{d}T_g/\mathrm{d}t) = \log (-\mathrm{d}\Theta/\mathrm{d}t) = K - ab/(b + \Theta) \quad (3)$$

where $\Theta = T - T_g$, $ab = 900$ °C, and $b = 51.6$ °C. Plotting log ($-$dΘ/dt) vs. $(b + \Theta)^{-1}$ (Figure 6) results in two straight lines, one describing most of the reaction, the other covering the highest conversion ranges. T_g at conversion zero, $T_{g,0}$, has to be known in order to transform these lines to the T_g vs. conversion plot (Figure 4). Again using $T_{g,0} = 207.5$ K, the slope obtained from Figure 6 ($ab = 943$ °C), and the known reaction kinetics,[6] the solid line in Figure 4 is calculated by eq 3.

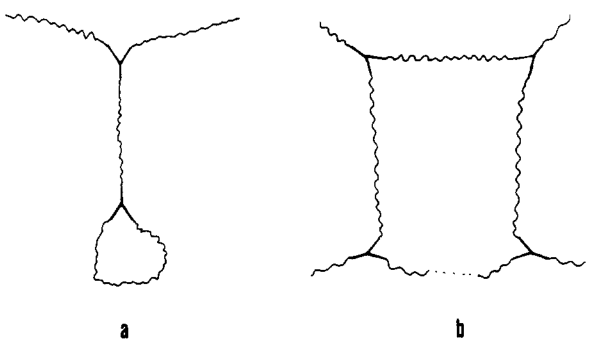

Figure 7. Types of rings formed in trifunctional networks: (a) smallest ring, elastically ineffective[17]; (b) large elastically effective ring.

The agreement between theory and experiment is quite remarkable, indicating that the reaction is mainly diffusion controlled. This is in agreement with the finding that the activation energy for the rate constant describing the reaction is 43 kJ mol^{-1}, which is close to the apparent activation energy of the diffusion coefficient of PPO($\bar{M}_n$ = 10 000) in a matrix of PPO($\bar{M}_n$ = 38 000 and $\bar{M}_w$ = 60 000): 43.9 kJ mol^{-1}.[13]

Above 80% conversion an additional reaction is superimposed on the diffusion-controlled reaction. This new process causes a change in reaction kinetics and has been interpreted as intramolecular reaction.[6] Short-chain segments which are responsible for intramolecular reactions are more mobile than whole chains which propagate intermolecular reactions.[12] Chain segments react faster whereas the intermolecular reaction is still diffusion controlled. However, before molecules with high molecular weights and high functionalities are present, intramolecular reactions are negligible.[14,15]

Generally the intramolecular reaction increases the cross-link density, thus increasing T_g. However, in our system the T_g increase slows down with increasing intramolecular reaction (Figure 4). As has been shown,[16,17] predominantly small loops are formed during the intramolecular reaction. In trifunctional networks the smallest loop possible leads to a dangling end containing two PPO chains (Figure 7a). Dangling ends do not contribute to an increase in the network T_g. On the contrary, they lead to plasticization due to increased free volume or more precisely due to a constancy of free volume.[18,21]

As originally suggested by Fox and Flory,[19] the glass transition temperature can be thought of as an iso-free volume state. In a curing system free volume is consumed by addition reactions of end groups to form linear copolymers and by cross-linking reactions which consume end groups and sites along the linear copolymer and additionally restrict the movement of the chains participating in the cross-link. The formation of a loop containing dangling ends consumes free volume linked with the chemical reaction. This does not restrict the movement of the chain as severely as a cross-link would. As long as branch points are not cross-link points (small molecular sizes), the change in free volume due to the change in chemistry (copolymerization) is the main influence of T_g. As cross-linking increases the restriction of chain movements leads to an enhanced T_g increase. It is at that stage that the contribution of dangling ends in lowering the T_g becomes important. This effect causes the second line in Figure 6 and the deviation from the calculated line at very high conversion in Figure 4. These deviations are consistent with studies showing that the depression of T_g in a network system by a given compatible diluent increases as the degree of cross-linking increases.[7]

Intramolecular Reactions in Other Curing Systems. Monte Carlo calculations by Romantsova et al.[20] predict autoacceleration of intramolecular reactions due to decreasing chain dimensions with increasing intramolecular cross-linking and thus increased functionality density. At high cross-link densities, however, the intramolecular reaction slows down. This is explained by the exhaustion of reactive groups. It could as well be explained (or caused) by steric restrictions imposed by existing cross-links. Intermolecular reactions are excluded in this model.

These findings may provide a clue as to why autoacceleration is found in some curing systems and not in others even though the model is obviously not appropriate to describe curing.

Besides the PPO–triisocyanate thermoset, one other system is reported to show an increase in reaction velocity in the postgel region.[21,22] This system consists of poly(ester triol) and diisocyanate. Both systems are comprised of relatively high molecular weight flexible prepolymers which are cured to networks with functionality 3. The gel point for both systems is above 70% conversion. Other thermosets normally show different characteristics including prepolymers which are not very flexible and with molecular weights <1000. Cross-link functionalities are higher than 3 and gel points are accordingly below 50% conversion.

Following Romantsova et al.,[20] Stepto,[15] and Stafford,[14] we can assume that in low-functionality and small-size molecules, intramolecular reaction is neither important nor autoaccelerated. At the gel point large molecules appear and intramolecular reaction should become important. The amount of intramolecular reaction will then depend on two factors: (1) the ratio of available intramolecular to available intermolecular reacting groups and (2) the accessibility of functional groups within large molecules to reactants bound to small molecules or, expressed in other terms, the screening of functionalities within large molecules from intermolecular reaction, thereby making these groups into intramolecular reacting groups.

Simple calculations according to the Flory–Stockmayer theory show that the number-average degree of polymerization at the gel point becomes smaller when the functionality increases. This means that the ratio of unreacted groups bound to large molecules (potential intramolecular reacting groups) to unreacted groups bound to small molecules is smaller for lower gel points, the occurrence of which is lower the higher the functionality. This suggests that intermolecular reactions beyond the gel point will be easier in higher functional systems. Furthermore, trifunctional cross-link points connected to long chains remain very flexible throughout the reaction (as long as $T_g < T_{cure}$). Higher functionalities and shorter chain lengths lead to mobility restrictions and thus decreased probability for any reaction including intramolecular reactions.

Although these explanations seem plausible, more experimental and theoretical data will be needed to understand the observed behavior satisfactorily.

The WLF Concept Applied to Other Curing Systems. The T_g increase during cure of epoxy systems is normally much higher than in the present case. Although these cures usually are accomplished at various temperature cycles, data of isothermally cured epoxies are available. In the early stages of these isothermal cures Θ is > 80 K and the reactions are kinetically controlled. As T_g increases so does the cross-link density bringing the reaction under diffusion control. The upper possible curing temperature is determined by the onset of degradation. Because the T_g's of fully cured epoxy systems are often very high there is not much difference between the isothermal temperature required for full cure and the degradation temperature.

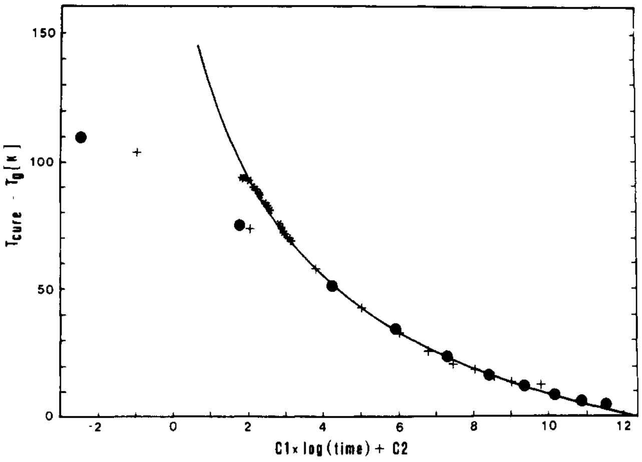

Figure 8. Master curve for isothermal cure of PPO1000–triisocyanate (*), CT200-HT901[5] (+), and CY207-HT903[5] (●).

The change in T_g during isothermal curing experiments should be describable by a WLF expression in the case of diffusion-controlled reaction. To obtain the time dependence of $\Theta = T_{cure} - T_g$, eq 3 has to be integrated, giving

$$t = -(b + \Theta)\exp(C - 2.303K) + 2.303ab\exp(-2.803) \times [\log C + C + C^2/(2(2!)) + C^3/(3(3!)) + ...] \quad (4)$$

with $C = 2.303\, ab/(b + \Theta)$, $a = 17.4$, and $b = 51.6$. The value of the convergent series in brackets depends only on Θ. If log (time) is plotted instead of time [both in arbitrary units] a change in K only moves the curve parallel to the log (time) axis. Converting the real time of the diffusion-controlled part of isothermal T_g vs. time plots to the log (time) scale a master curve should be obtained. Figure 8 shows that this is found for our data (*) and the data (+ and ●) of Stevens and Richardson[5] (their Figures 4 and 5). The systems described by them are anhydride-cured diglycidyl ether of bisphenol A type epoxy resins (Ciba-Geigy's CT200-HT901 (+) and CY207-HT903 (●)). K was arbitrarily chosen as 5.3, the value obtained for the PPO1000–triisocyanate system. The congruence of the values of the epoxy resins for $\Theta \leq 60$ K is quite good. At higher Θ the cure of these systems is obviously kinetically controlled.

It is interesting to see that the WLF approach predicts an increase in T_g even at $T_g(\Theta = 0)$. However, the data seem to show a smaller increase of T_g very near to $\Theta = 0$.

Conclusions

The investigation of model network cure provides information about the nature of mechanisms leading to higher glass transition temperature by curing. A general pattern is found for isothermal cure. At low conversion (large Θ) curing is governed by kinetic-controlled reactions. With increased T_g the reactions become dominated by diffusion-controlled processes. The data can then be fitted to a master curve. Autoaccelerated intramolecular reaction can be superimposed on the diffusion-controlled, mainly intermolecular processes. This is found only in highly flexible systems with low cross-link densities and low cross-link functionalities above the gel point which occurs at high conversion. The exact mechanism of the autoaccelerated process will need further investigations.

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Registry No. (α,ω-Dihydroxypoly(propylene oxide))·(tris(isocyanatophenyl) thiophosphate) (copolymer), 88546-51-4; araldite CT 200, 25085-99-8.

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Model for the Clustering of Multiplets in Ionomers

Bernard Dreyfus

Groupe de Physico-Chimie Moléculaire, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble Cédex, France.

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ABSTRACT: A new model for the clustering of charges in ionomers is presented. The basic idea is that, due to the strong electrostatic interactions, the multiplets of charges build a kind of structure, with a geometry that takes into account the presence of the polymeric material. The result is a cluster which, for a given material, is independent of the concentration of charges. It is shown that the multiplets are very likely quadruplets. It is also shown that the large cations produce bigger clusters. The state of the chains inside the matrix is discussed and it is suggested that the clusters are arranged in hypercrystallites, with a diamond structure. This allows for the interpretation of the central peak observed in diffraction experiments. A preliminary discussion of the first step of hydration is also presented.

1. Introduction

Ionomers are defined as copolymers containing predominantly linear nonpolar backbones and less than about 10 mol % of charged neutralizable side groups. Their properties are dominated by the existence of long linear polymeric chains which are strongly cross-linked by the electrostatic forces between the charged monomers. We exclude here materials such as "Nafions", perfluorinated ionomers where the charged units are at the end of rather long side pendant chains. In these materials the interaction between the electrical charges and the main chain is much weaker, and they may display structures differing from those discussed here.

In the last 15 years, many experimental studies have been conducted on ionomers. We refer the reader to three review articles[1-3a] and one recent paper devoted to the structure of the ionomeric membranes[3b] which give an extensive description of these works as well as the different models that have been proposed. The studies include a large variety of monomers (ethylene, butadiene, styrene, etc.) as well as charged acids (carboxylic, methacrylic, sulfonic, etc.) and neutralization cations (Na, Cs, Zn, Fe, ...). Although much progress has been made, it is generally accepted that the structure of these compounds is still poorly understood. The objective of this paper is to present a model which is mathematically simple and yet quantitatively predictive.

In a pioneer work Eisenberg[4] showed that the condensation of charges is a two-step process. The basic *ionic pairs* consisting of one anion (the acid) and a neutralizing charge (the cation) are associated with a few other pairs, more or less in contact, to form a *multiplet* resulting in strong cross-linking of different polymer chains, or different segments of one chain. We call the electric interaction responsible for the formation of the multiplets the *primary* electrostatic energy. This primary energy of interaction is an important fraction of the total energy of a basic pair. In a vacuum this energy is 100 kcal or 185 times $k_B T$ at room temperature for two point charges 3 Å apart. Such a huge energy can easily stress the polymer chains during cross-linking since the energy needed to produce a strong deformation of one segment of a chain is a only a few $k_B T$. What limits the size of the multiplet is the steric hindrance since each ionic pair is coated by neutral monomers. This prevents the growth of the multiplet beyond a certain size, except in special cases, which will not be considered here, such as a lamella where a linear agglomeration of the basic pairs is possible. We shall call an object made of k basic pairs a "$2k$-plet". $k = 1$, the basic pair itself, is an electrical dipole; $k = 2$, corresponding to two basic pairs, is a quadrupole. Because of the steric hindrance, it is likely that in most ionomers k is a rather small number, probably smaller than 4, and most likely equal to 2 (dimerization). Being electrical $2k$-poles, coated with neutral materials, these multiplets still interact among themselves. We call this corresponding energy the *residual* energy of interaction. This energy can be larger than $k_B T$. For example, two basic dipoles, built

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