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Determination of the Repartition of Monomers Between Sol and Gel Fractions in Copolycondensate Glycerol/Azelaic Acid by Radioassay

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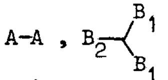
ABSTRACT : The distribution of the monomers between sol and gel fractions, theoretically forecasted from network formation theory, is experimentally determined in glycerol/azelaic acid system with tritium labeled glycerol by radioassay.

INTRODUCTION :

In multicomponent systems, network formation theories give the repartition of the different monomers between the sol and gel fractions as a function of the parameters of reaction components (composition of the initial system, functionality and reactivity of the components, etc...) and the reaction extent. In the system glycerol/azelaic acid, the isotopic label of one of the monomers was proving an effective and precise experimental way in order to determine the distribution of the monomers between the sol and gel fractions.

THEORETICAL PART :

Examine the copolycondensation of A-monomers with B-monomers schematically depicted as :



$$A{-}A\ ,\ B_2{-}\!\!<\!\begin{smallmatrix}B_1\\B_1\end{smallmatrix}$$

B_1 and B_2 denoting two kinds of B-functional groups having intrinsically unequal reactivity.

Let n_A and n_B be the respective molar fractions of the A-monomers and B-monomers having respectively the molecular weight M_A and M_B, and let M_E be the molecular weight of by-product (here, M_A=188, M_B= 92, M_E=18).

Let p_{AB1}, p_{AB2} be the fractions of A-sites having reacted respectively with B_1- sites and B_2-sites ; p_{B1A}, p_{B2A}, the respective fractions of reacted B_1 and B_2 sites. The total fractions of reacted A and B-sites may be written :

$$p_A=p_{AB1} + p_{AB2} \qquad p_B=(2p_{B1A} + p_{B2A})/3$$

The stoichiometric ratio $r=2n_A/3n_B$ gives relations between

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the reaction extents relative to A and B-sites :

$$p_B = rp_A \qquad 2p_{B1A}=3rp_{AB1} \qquad p_{B2A}=3rp_{AB2}$$

If we assume that the copolycondensation is 1st order in B-sites and any order in A-sites, the kinetic equations (1) lead to the relation :

$$(1-p_{B1A})=(1-p_{B2A})^{\rho} \quad \text{, with } \rho=k_1/k_2$$

where k_1, k_2 are respectively the rate constants of reaction of a B_1-site and B_2-site with an A-site ($\rho=4$ at 160°C with glycerol).

If we assume that the number of intramolecular reactions of finite size molecules is negligibly small, the considered reaction leads to a network whose local connectivity is tree-like. Such representation of polymer network structure is given by the graph-like-state theory developed by Gordon and coworkers (2).

The statistical parameters for the sol and gel fractions can be computed from the probabilities that an A-site (π_A), a B_1-site (π_{B1}) and a B_2-site (π_{B2}), selected at random, lead to finite chains. These probabilities may be derived as a function of reaction extent from the system of implicit equations (3).

$$\pi_{B_1}=p_{B1A}\pi_A + 1-p_{B1A} \quad ; \quad \pi_{B2}=p_{B2A}\pi_A + 1-p_{B2A}$$

$$\pi_A = p_{AB1}\pi_{B1}\pi_{B2} + p_{AB2}\pi_{B1}^2 + 1-p_A$$

Each of those probabilities is made up of two contributions : the probability that the considered site is found reacted and led to finite chains, plus the probability that it is found unreacted. Analogous arguments were developed recently by different authors (4,5).

A monomer will be part of the sol if all its sites lead to finite chains.

The molar fraction $\nu_{A,s}^{(k)}$ of A-monomers belonging to the sol and having k(=0,1,2) reacted A-sites may be written :

$$\nu_{A,s}^{(k)} = \binom{2}{k} [\pi_A-(1-p_A)]^k(1-p_A)^{2-k} \quad \text{where } \binom{n}{p}=n!/[p!(n-p)!]$$

The molar fraction $\nu_{B,s}^{(k_1,k_2)}$ of B-monomers belonging to the sol and having k_1(=0,1,2) reacted B_1-sites and k_2(=0,1) reacted B_2-sites is :

$$\nu_{B,s}^{(k_1,k_2)}=\binom{2}{k_1}(p_{B1A}\pi_A)^{k_1}(1-p_{B1A})^{2-k_1}\binom{1}{k_2}(p_{B2A}\pi_A)^{k_2}(1-p_{B2A})^{1-k_2}$$

Assuming that whenever one AB bond is made, A and B-sites contribute respectively mass M_{EA} and M_{EB} to the condensate (with $M_E=M_{EA}+M_{EB}$), the weight fraction of the A-monomers in the sol is:

$$w_{A,s}=\frac{n_A\sum\limits_{k=0}^{2}\nu_{A,s}^{(k)}(M_A-kM_{EA})}{\bar{M}_{no}-2p_AM_E}=\frac{n_A\pi_A\{\pi_AM_A-2[\pi_A-(1-p_A)]M_{EA}\}}{\bar{M}_{no}-2p_AM_E}$$

where $\bar{M}_{no}=n_AM_A+n_BM_B$

On another way :

$$w_{A,s}=\frac{n_A[\pi_A^2M_A-2p_{A,s}M_{EA}]}{\bar{M}_{no}-2p_AM_E}\qquad p_{A,s}=\sum_{k=o}^{2}k\nu_{A,s}^{(k)}=\pi_A[\pi_A-(1-p_A)]$$

where $p_{A,s}$ is the fraction of reacted A-sites belonging to the sol.

The weight fraction of the B-monomers in the sol is :

$$w_{B,s}=\frac{n_B\sum\limits_{k_1=o}^{2}\sum\limits_{k_2=o}^{1}\nu_{B,s}^{(k_1,k_2)}[M_B-(k_1+k_2)M_{EB}]}{\bar{M}_{no}-2p_AM_E}=\frac{n_B[\pi_{B1}^2\pi_{B2}M_B-3p_{B,s}M_{EB}]}{\bar{M}_{no}-2p_AM_E}$$

where $p_{B,s}$ is the fraction of reacted B-sites in the sol.

As $2n_Ap_{A,s}=3n_Bp_{B,s}$, the total sol fraction $w_s=w_{A,s}+w_{B,s}$ may be written :

$$w_s=\frac{n_A\pi_A^2M_A+n_B\pi_{B1}^2\pi_{B2}M_B-2\pi_A[\pi_A-(1-p_A)]M_E}{\bar{M}_{no}-2p_AM_E}$$

To illustrate, in a more general way, the composition of the sol fraction with regard to the composition of the whole copolycondensate, with different stoichiometric and reactivity ratios (r,ρ), we give in Fig. 1 and 2 the variation of the quantity $(n_{B,s}/n_s)/n_B$ as a function of reaction extent p_A.

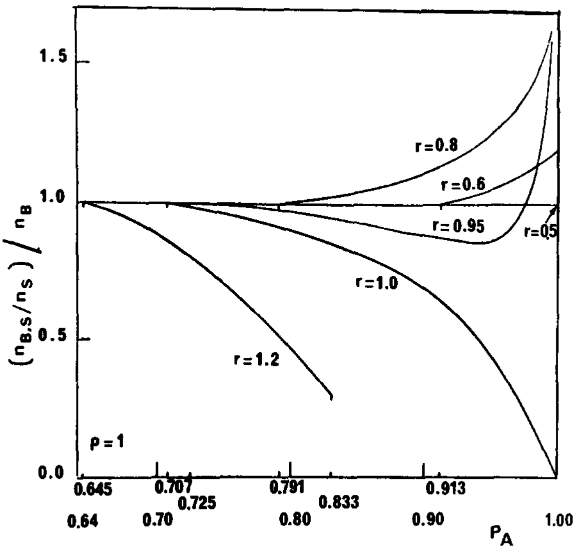

Fig. 1 : Molar fractions ratio sol/(sol+gel) of the B-monomers for various stoichiometric ratios r versus reaction extent p_A (equireactive system)

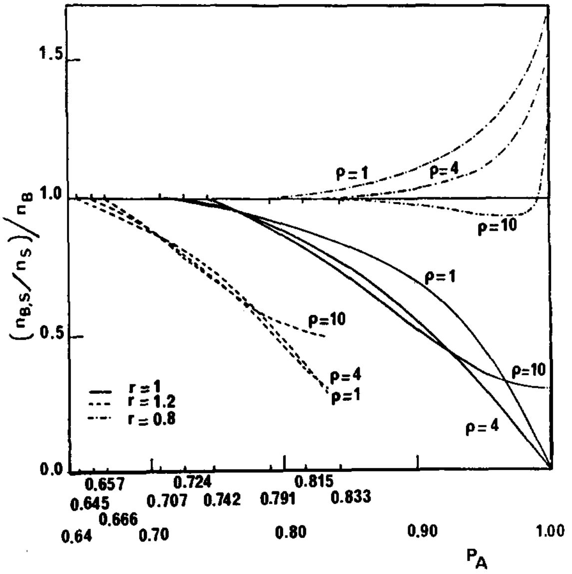

Fig. 2 : Molar fractions ratio sol/(sol+gel) of the B-monomers for various reactivity ratios ρ versus reaction extent p_A

EXPERIMENTAL PART

Copolycondensates are prepared by reacting azelaic acid and glycerol in stoichiometric ratio at 160°C under nitrogen atmosphere. Glycerol contains 0.01 ppm tritum labeled glycerol, whose specific activity (1µCi/g) is determined after addition of scintillator solution, by using liquid scintillation counting.

To obtain a large range of different sol fractions, copolycondensations are made with and without catalyst (p-toluene sulfonic acid). In catalysed systems, the reaction rate is accelerated (in half an hour, the gel point is reached), so only low sol fractions may be practically obtained, whereas uncatalysed reactions which are slower (the gel point is reached after four hours) allow one to obtain sol fractions near after the threshold of gelation.

Each copolycondensate is divided in two parts : the first part (i) is used to determine the composition of the whole system (consequently its stoichiometry) and the second part (ii), the sol weight fraction and its composition. Each party is itself divised into two fractions, to verify the reproductibility of the results.

Each of the fractions of the first part (i) are solubilized with a solution of a quaternary ammonium base in toluene. After addition of scintillator solution, glycerol content m_B (mmol./g of copolycondensate) is determined by radioassay.

From each of the fractions of the second part (ii), the sol fraction is extracted with methyl ethyl cetone (MEC) until constant weight at room temperature (on an average, 4 to 5 two days extractions are necessary). So, the sol weight fraction w_s may be determined gravimetrically. Then,these fractions are solubilized with the minimum of MEC and glycerol content m_B (mmol./g of sol) is determined by radiossay.

For every radioassay, corrections of quenching are made by using a calibration curve obtained from external standardization method.

RESULTS AND DISCUSSION

Fig. 3 and 4 give experimental and theoretical glycerol contents (mmol./g) in the total system m_B (curve 1) and in the sol fraction m_B (curve 2) versus gel weight fraction w_g in catalysed and uncatalysed reactions.

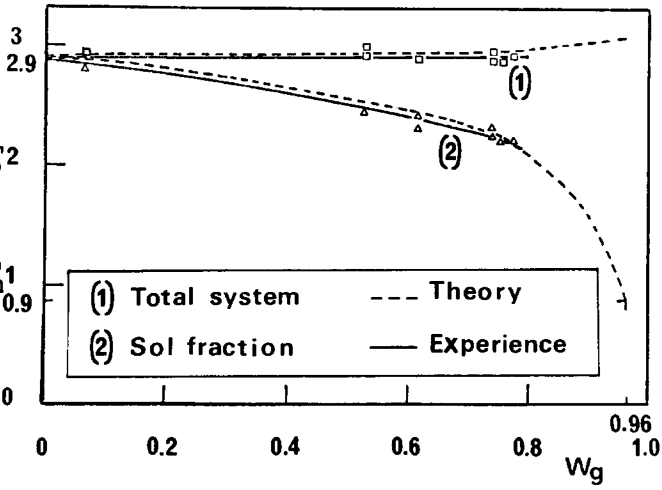

Fig. 3 : Variation of glycerol content m_B in the total system (curve 1) and in the sol fraction (curve 2), for *catalysed* copolycondensates glycerol/azelaïc acid, versus gel weight fraction w_g.

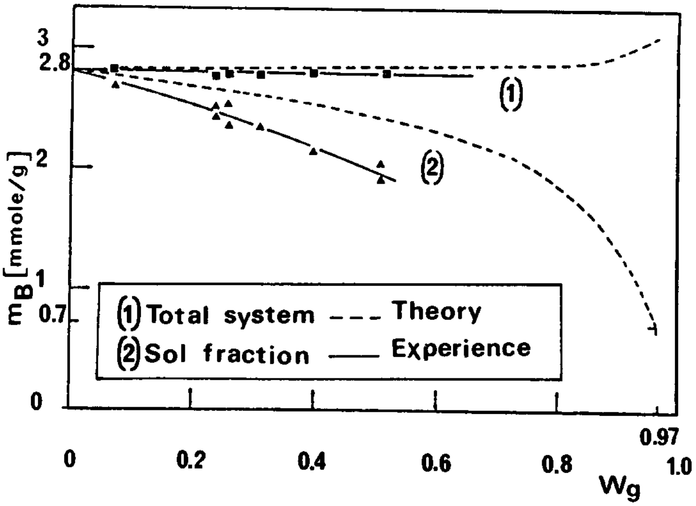

Fig. 4 : Variation of glycerol content m_B in the total system (curve 1) and in the sol fraction (curve 2), for *uncatalysed* copolycondensates glycerol/azelaïc acid, versus gel weight fraction w_g.

From stoichiometric mixtures, all the samples show, after the gel point, identical, but more than one stoichiometric ratios whatever the amount of the sol fraction is ; so, a preferential departure of glycerol could take place during the pregelation. That stoichiometric ratio (1.17 in catalysed reactions, 1.23 in uncatalysed reactions) increases with pregelation duration. The theoretical curves deal with copolycondensate triol/diacid having respectively the above stoichiometric ratios and a reactivity ratio $\rho=4$.

The composition of the sol fraction for catalysed reactions (Fig. 3) shows a good agreement of experimental results with theory. For uncatalysed reactions (Fig. 4), the glycerol content is lower than the theoretical forecasts. This discrepancy could be partly attributed to a more important amount of secondary reactions in uncatalysed systems as a result of a longuest reaction duration and a largest excess of azelaic acid.

CONCLUSION

This preliminary work clearly shows that the study of isotopic labeled monomers systems gives informations about the repartitions of the monomers between sol and gel fractions. Notice that in the theoretical part, unequal reactivity of functional groups have been taken into account, but intramolecular reactions leading to uneffective cycles and secondary reactions have been neglected. This study has been managed with system whose choice has been governed by the readily commercial availability of the tritium labeled polyol (glycerol). This fruitful technic would have to be enlarged to either more ideal or more sophisticated systems in order to test some qualitative aspects of network theories.

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