

Kinetics of Epoxy Resin Synthesis on the Basis of GPC Measurements

INTRODUCTION

Recently considerable research work has been done on the molecular mass distribution (MMD) of epoxy resins synthesized by different methods. For this purpose gel permeation chromatography (GPC) was mostly used. Batzer and Zahir¹⁻⁴ gave systematic comparison of the theoretically calculated and experimental MMDs of resins manufactured by the taffy and the advancement processes. Semiquantitative kinetics data were also presented by these authors⁴ for the taffy process. A similar investigation is presented in this note using GPC to follow the elemental steps of the resin forming reaction in the case of the advancement process. The calculation used is the same as that proposed by Ravindranath and Gandhi.⁵

EXPERIMENTAL

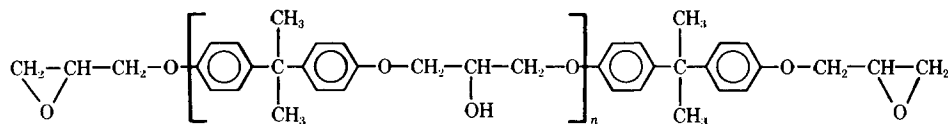
As epoxy component pure diglycidyl ether of bisphenol A (DGEBA) was used (Epon 825, Shell Chem. Co.). The other component, i.e., bisphenol A, can also be regarded as practically pure (Mitsui Co.). The molar ratio *r* of bisphenol A to DGEBA was chosen to be 0.5. The reaction was carried out at 145–150°C in the presence of tetramethyl ammonium chloride as catalyst under the conditions described in the patent literature.⁶

The epoxide content of the samples was measured by potentiometric titration with perchloric acid.⁷ For the determination of phenolic hydroxyl content a spectrophotometric method was adopted.⁸

The GPC measurements were performed by an instrument equipped with three Styrogel columns of nominal porosities 250, 500, and 2000 Å, packed by Waters Assoc. and a column packed with Sephadex LH-20 gel, connected in series. The samples were dissolved and eluated in tetrahydrofuran at ambient temperature, and a differential refractometer was used as concentration detector. According to our experience the refractive index of the components of different molecular masses is constant in this range. The rough chromatograms were corrected for zone spreading by using a combination of the methods of Ishige et al.⁹ and Pierce and Armonas.¹⁰ In order to improve the signal-to-noise ratio, the correction was applied to the average of the curves obtained from two to four parallel runs.

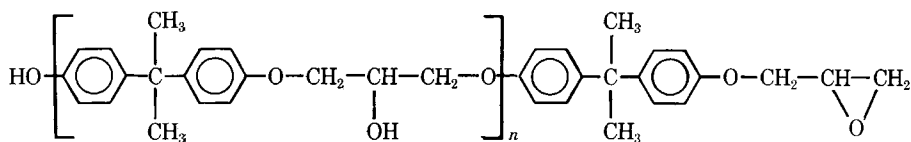
RESULTS AND DISCUSSION

From a kinetics point of view, the advancement process is simpler than the taffy one, since there is no elimination step and the reaction takes place in a homogeneous phase. Furthermore, if the starting components are pure and the epoxide groups react with the phenolic hydroxyls only, at the molar ratio in question the epoxy resin formed consists of oligomers having the structural formula EE_n :

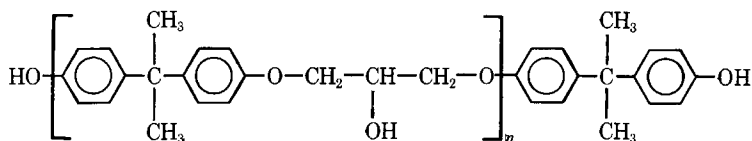


During this step-growth polymerization two types of intermediary products occur with the structural

formulae EP_n and PP_n , where E and P denote the epoxide and the phenolic end-groups:



and



It is evident from the stoichiometry that n is always an even number for EE_n and PP_n , while only odd EP_n mers can exist. If $n = 0$, EE_n represents DGEBA and PP_n represents bisphenol A. The advantage of using pure DGEBA lies in the fact that between the GPC peaks of even epoxymers the intermediates can be separately observed, at least in the region of low molecular mass.

Table I provides the change in the concentration of the reacting groups in the reaction mixture. It can be seen that the phenolic hydroxyl content becomes lower than 1 meq/100g in five hours, while the equivalent amount of epoxide groups is consumed in about two hours. At the end of the reaction the epoxide content of the resin is lower than the theoretically predicted value by 12 meq/100g. This difference suggests that about 6% of the epoxide groups was consumed in a competing side reaction. In the literature this side reaction is assumed to be either that of the epoxide and the alcoholic hydroxyl groups or the anionic polymerization of epoxide groups.

Figure 1 shows the MMDs of the polymerization products at different times during the reaction. The peaks of bisphenol A (PP_0), DGEBA (EE_0), and that of the higher epoxymers up to EE_6 are

TABLE I
Concentration of Functional Groups at Given Reaction Times

Reaction time (h)	Concentration (meq/100g)	
	Epoxide	Phenolic hydroxyl
0.0	441	221
0.5	355	135
1.0	281	73
1.5	248	38
2.0	222	17
5.0	208	0.5

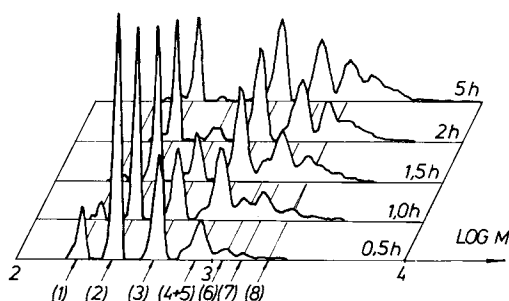


Fig. 1. Change in molecular mass distribution of the reaction mixture at increasing reaction time: (1) PP_0 , $M = 228$; (2) EE_0 , $M = 340$; (3) EP_1 , $M = 568$; (4) PP_2 , $M = 796$; (5) EE_2 , $M = 908$; (6) EP_3 , $M = 1136$; (7) EE_4 , $M = 1476$; (8) EE_6 , $M = 2044$.

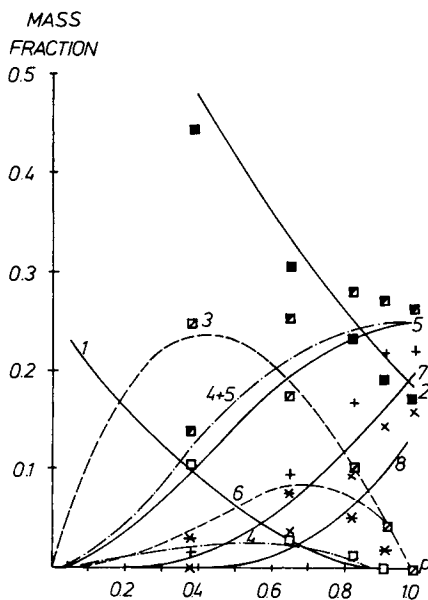


Fig. 2. Mass fractions of components present in the polymerization as a function of the extent of reaction p . The full and dotted lines are theoretically deduced, the points represent the experimentally obtained values: (1) \square PP_0 , (2) \blacksquare EE_0 , (3) \square EP_1 , (4) + (5) \blacksquare $PP_2 + EE_2$, (6) $*$ EP_3 , (7) + EE_4 , (8) \times EE_6 .

separated, and the peaks of EP_1 and EP_3 also appear individually. However, the first intermediate with two phenolic endgroups, PP_2 , shows only a shoulder on the left side of the peak of EE_2 , as could be expected.

With the aid of a modified version¹¹ of Flory's theory the mass fractions of each component were computed as a function of the extent of reaction p . In Fig. 2 these theoretical curves are shown together with the experimental data obtained from GPC measurements, where p was calculated according to the reacted phenolic hydroxyl groups (see Table I). It can be seen that the DGEBA content of the samples is somewhat lower than the theoretically deduced values, while the ratio of the first three epoxymers is higher. At the same time the values measured for bisphenol A and EP_n intermediates fit the curves well.

Batzer and Zahir¹ have found that the agreement between the theoretical and experimental distributions in the case of the advancement process holds only if the calculation was performed for resins having epoxide values lower than the measured ones by 10 meq/100g. We have also tried to change the parameter r in the calculation of theoretical curves, but the best agreement was obtained using the real value of 0.5.

Taking into consideration the DGEBA content of the reaction mixture, nearly the same extent of side reaction can be concluded from the difference between the theoretical and experimental fractions as from the measurement of functional groups. It may be assumed that the increase of EE_2 , EE_4 , and EE_6 fractions is connected with the decrease of DGEBA content: since the products of side reaction and EE_n^* oligomers can have similar molecular masses and hydrodynamic volumes, they eluate together in GPC. However, by supposing the side reaction between the alcoholic hydroxyl and epoxide groups the good agreement between the experimental and theoretical values for EP_n intermediates as well as the increased EE_2 fraction cannot be explained. For this reason we believe that the side reaction is probably the anionic polymerization of DGEBA, as has already been demonstrated by Lidarik.¹²

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I. ANTAL
L. FÜZES
G. SAMAY
L. CSILLAG

Research Institute for Plastics
Budapest, XIV. Hungária krt. 114
Hungary, 1950

Received October 16, 1980
Accepted March 2, 1981