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Character of Active Centers in the Copolymerization of Epoxides with Cyclic Anhydrides

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ABSTRACT

The conductivity of different catalytic and copolymerization systems which were used for the copolymerization of epoxide with cyclic anhydride catalyzed by a tertiary amine, ammonium salt, alkali salt, and the system tert-amine-proton donor compound was conductometrically investigated in different solvents at 120°C. Measurements of the conductivity of the system epoxide-anhydride-tertiary amine as well as that of components and binary solutions indicate that a considerable increase in conductivity appears only in a ternary system. The temporal course of conductivity of the reaction system indicates the ionic character of copolymerization while the conductivity plot shows a maximum. The increase in conductivity in the initial stage of reaction is interpreted as a result of the formation of active centers before reaching a stationary concentration (induction period); the decrease in conductivity is regarded as a consequence of the reduced mobility of macroins due to the increase in molecular weight and macroviscosity of the system and to the dissolving ability of solvent. The absolute value of conductivity of the copolymerization system depends on the polarity of solvent and increases with dielectric constant. Similar results were obtained with the tertiary amine-proton donor catalyst system. The catalytic effect of alkali and ammonium salts brings about rapid dissociation and increase in conductivity of the copolymerization system. As in catalysis by tertiary amine, the decrease in conductivity is attributed to the decrease in mobility of ions and to a solvent effect. Comparison of maximum conductivities with rate constants for copolymerization points out that the ion pairs of active centers as well as the dissociated salt have a catalytic effect.

INTRODUCTION

There are several views on the character of active centers, depending on the kind of catalyst in the copolymerization of epoxides with cyclic anhydrides. For the copolymerization of epoxides, cyclic carbonates, or sulfites of diols with cyclic anhydrides catalyzed by alkali salts, the active center shows anionic character [1] and is produced by dissociation of the catalyst in polymerization mixture. For the copolymerization catalyzed by tertiary amines, it is assumed that either the active center shows anionic character [2-4] or the tertiary amine is operative in a ternary complex produced by interaction among tert-amine, proton donor compound, and epoxide [5]. It is assumed that the active center of anionic character originates from the direct interaction between the tertiary amine and the anhydride, giving a zwitterion (of betainelike structure) [2] or from the primary interaction between tertiary amine and proton donor compound, giving rise to a binary associated complex which, in subsequent reaction, yields again the zwitterion stabilized by proton donor compound [3]. A different mode of formation of active centers has been suggested by Feltzin [4], who assumes that the tertiary amine is activated by a proton donor compound to give an anionic salt which forms the growth active center of anionic character in the presence of anhydride. Nevertheless, there is no evidence which could confirm the view on the character of the active center. Only the increase in the rate of copolymerication due to increasing dielectric constant of solvent [5] could speak for an anionic mechanism.

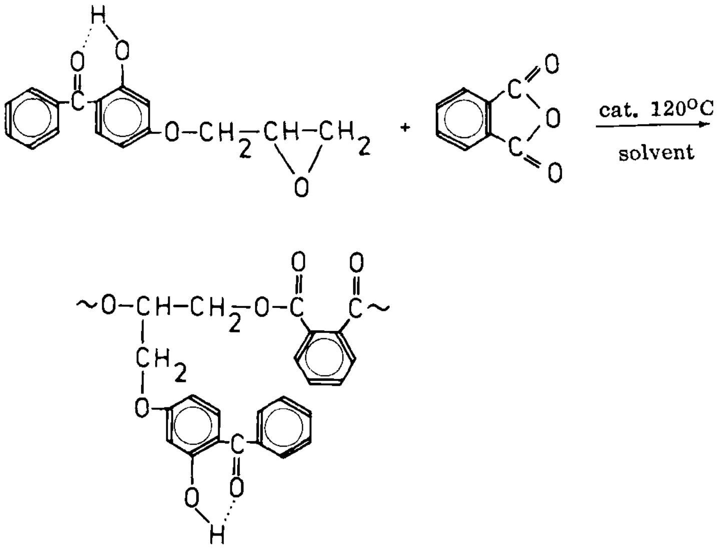
In this study, we measured the conductivities of solutions of individual components of the polymerization system. For these measurements, we used 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) as epoxide, phthalanhydride (PA) as anhydride, tri-n-hexylamine (THAm) as tertiary amine, benzoic acid (BA) and cyclohexanol as proton donor compounds, cetyltrimethylammonium bromide (CAB) as a quaternary ammonium salt, and potassium benzoate (BzK) as alkali salt.

EXPERIMENTAL

2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone was prepared according to the literature [6, 7]. The recrystallized product with mp 100-100.5°C was used. Phthalanhydride (Lachema, N. E., Brno, Czechoslovakia) was purified by sublimation in nitrogen. Tri-n-hexylamine (Fluka A. G., Switzerland) was purified by distillation under reduced pressure. Benzoic acid, cyclohexanol, and cetyltrimethylammonium bromide (Lachema, N. E., Czechoslovakia) were analytical grade chemicals which were used without any purification. Potassium benzoate was prepared by neutralizing benzoic acid with potassium hydroxide. The solvents were purified by the usual procedures [8]. The conductivities were measured at 120°C in a reactor equipped with a thermometer and stirrer by means of a conductivity meter, type OK-102 (Radelkis, Hungary) equipped with a conductivity cell (OK-902, Radelkis, Hungary).

RESULTS

The conductivities of individual components of the polymerization system used for the copolymerization of HEPBP with PA catalyzed by tertiary amine [Eq. (1)] in the presence or absence of proton donor



(1)

compounds or ammonium or alkali salt were measured in some solvents of different polarity at 120°C. The selection of components of the investigated systems and the conditions of measurement were determined by the conditions of polymerization [9].

The conductivity of pure o-xylene on drying with sodium and rectification was 2.7×10^{-9} S/m and did not change even after 4 hr, similarly as the identical values of conductivity of the solutions of HEPBP (0.5 mole/liter) and of PA (0.5 mole/liter) in o-xylene. The conductivities of the xylene solution of THAm (0.025 mole/liter 2.7×10^{-9} S/m) and of the system containing 0.025 mole/liter of CAB (4.1×10^{-9} S/m) were constant for 4 hr (CAB is sparingly soluble in o-xylene). The conductivity of the solution of BA (0.025 mole/liter) in o-xylene (2.7×10^{-9} S/m) did not change during 2 hr, even after the additions of THAm (0.025 mole/liter) and HEPBP (0.5 mole/liter). No increase in conductivity was observed until PA (0.5 mole/liter) was added. An addition of THAm (0.025 mole/liter) brings about a gradual increase in conductivity in the systems containing PA (0.5 mole/liter) (Fig. 1, curve 2). The simultaneous addition of THAm (0.025 mole/liter) and BA (0.025 mole/liter) to the solution of PA (0.5 mole/liter) first produces an increase in conductivity to approximately twice the original value which takes place in the course of 5 min (8.5×10^{-9} S/m) (Fig. 1, curve 4). Afterwards, there follows a practically linear, slow increase in conductivity which reaches a value of 3.0×10^{-8} S/m in 180 min. An analogous situation arises if cyclohexanol is used (0.025 mole/liter) (Fig. 1, curve 3), except that the slope of linear region is smaller. For the system containing PA (0.5 mole/liter) and CAB (0.005 mole/liter) in o-xylene, the conductivity plot shows a similar character, only the initial rise is greater than for the preceding systems (Fig. 1, curve 5). The solutions of HEPBP are less sensitive to additions of catalysts. The solution of HEPBP (0.5 mole/liter) and THAm (0.025 mole/liter) shows almost a linear increase in conductivity with very small slope from the initial value of 3.4×10^{-9} S/m (Fig. 1, curve 1).

The conductivity measurements in ternary solutions containing HEPBP (0.5 mole/liter), PA (0.5 mole/liter), and THAm (0.025 mole/liter) in o-xylene show an initial increase in conductivity; after about 110 min the curve reaches the maximum (9.4×10^{-8} S/m). Afterwards, the conductivity of the solution decreases exponentially (Fig. 2, curve 1). The plots for equal solution containing BA (0.025 mole/liter) or cyclohexanol (0.025 mole/liter) show analogous character (Fig. 2; curves 2 and 3). Only the time necessary to attain the conductivity maximum changes, while the differences between the maximum values of conductivity are small. In the ternary system of HEPBP (0.5 mole/liter), PA (0.5 mole/liter), and CAB (0.005 mole/liter) dissoved in o-xylene, the maximum conductivity is reached after 5 min during the dissolution of catalyst; and afterwards, it decreases exponentially

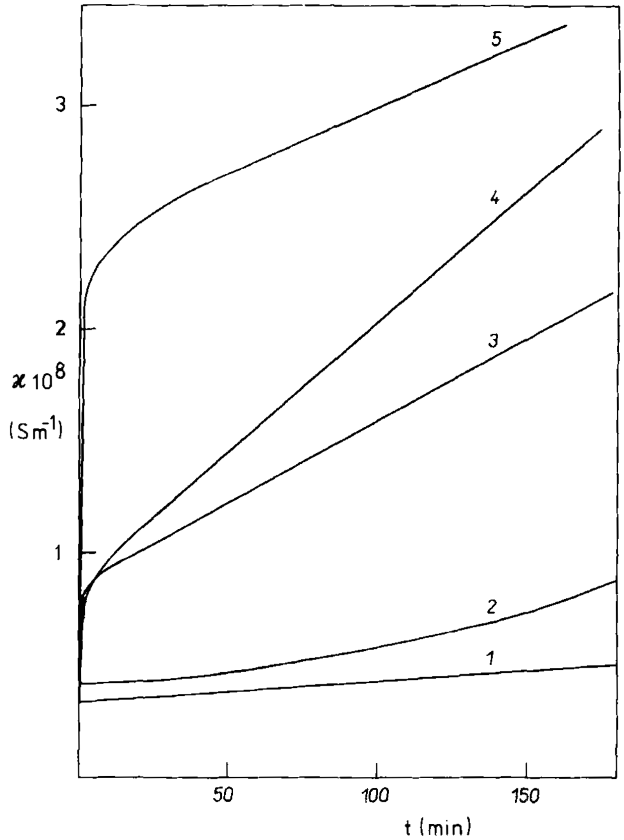


FIG. 1. Conductivity curves of binary and ternary mixtures of the copolymerization system HEPBP-PA in o-xylene at 120°C: (1) HEPBP (0.5 mole/liter), THAm (0.025 mole/liter); (2) PA (0.5 mole/liter), THAm (0.025 mole/liter); (3) PA (0.5 mole/liter), THAm (0.025 mole/liter), cyclohexanol (0.025 mole/liter); (4) PA (0.5 mole/liter), THAm (0.025 mole/liter), BA (0.025 mole/liter); (5) PA (0.5 mole/liter), CAB (0.005 mole/liter).

with time (Fig. 2, curve 4). In this case a comparable maximum value of conductivity (1.16×10^{-7} S/m) was found by using a five-times lower concentration of catalyst than it was necessary in the case of tertiary amine.

The time interval necessary to attain the maximum conductivity in

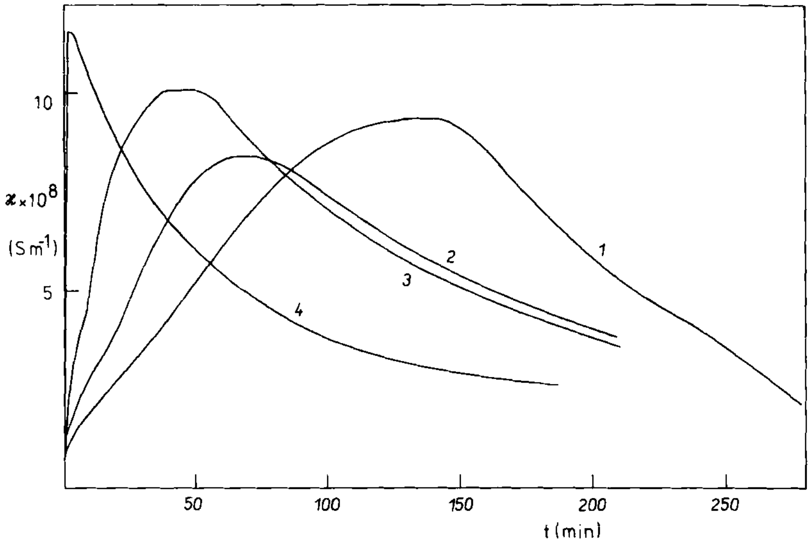


FIG. 2. Conductivity curves of the copolymerization of HEPBP (0.5 mole/liter) with PA (0.5 mole/liter) in o-xylene at 120°C: (1) THAm (0.025 mole/liter); (2) THAm (0.025 mole/liter), cyclohexanol (0.025 mole/liter); (3) THAm (0.025 mole/liter), BA (0.025 mole/liter); (4) CAB (0.005 mole/liter).

ternary polymerization systems is related to the duration of the induction period of the copolymerization of HEPBP with PA [9].

Conductivity measurements carried out with the system HEPBP-PA-THAm (0.5-0.5-0.025 mole/liter) dissolved in chlorobenzene have shown that the character of conductivity curve is similar to that found for this system dissolved in o-xylene, only the value of maximum conductivity is about five times as high (5.1×10^{-7} S/m) and is attained after a shorter time (Fig. 3, curve 1). If 1,1,2,2-tetrachloroethane is used as a solvent instead of o-xylene or chlorobenzene, the course of conductivity of equal system is quite different. As is obvious from Fig. 3 (curve 2), the conductivity of the polymerization system rises abruptly and subsequently reaches a constant value (1.3×10^{-6} S/m).

If BzK (0.005 mole/liter) is used as a catalyst and nitrobenzene as a solvent, the course of conductivity curve is analogous to that established for the polymerization of HEPBP with PA catalyzed by THAm in 1,1,2,2-tetrachloroethane. After a rapid increase in conductivity which is evidently related to the dissolution of BzK in the polymerization solution, the maximum conductivity is attained.

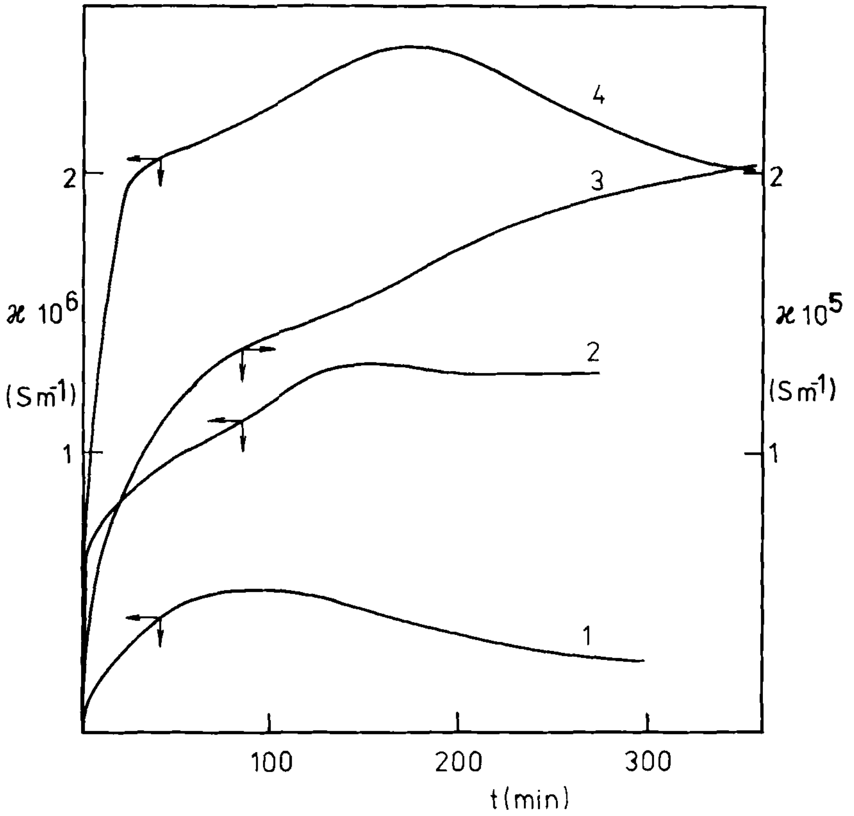


FIG. 3. Conductivity curves of the copolymerization of HEPBP (0.5 mole/liter) with PA (0.5 mole/liter) in different solvents catalyzed by THAm and BzK at 120°C: (1) THAm (0.025 mole/liter), chlorobenzene; (2) THAm (0.025 mole/liter), 1,1,2,2-tetrachloroethane; (3) THAm (0.025 mole/liter, nitrobenzene; (4) BzK (0.005 mole/liter), nitrobenzene.

Afterwards, a slight decrease appears and the conductivity settles at a constant value of 2.0×10^{-6} S/m (Fig. 3, curve 4).

If THAm is used as a catalyst in the nitrobenzene solution of HEPBP (0.5 mole/liter) and PA (0.5 mole/liter), a considerable initial increase in conductivity appears. The conductivity reaches an order of 10^{-5} S/m. After 100 min, an inflection point appears on the conductivity curve. The conductivity continues to increase

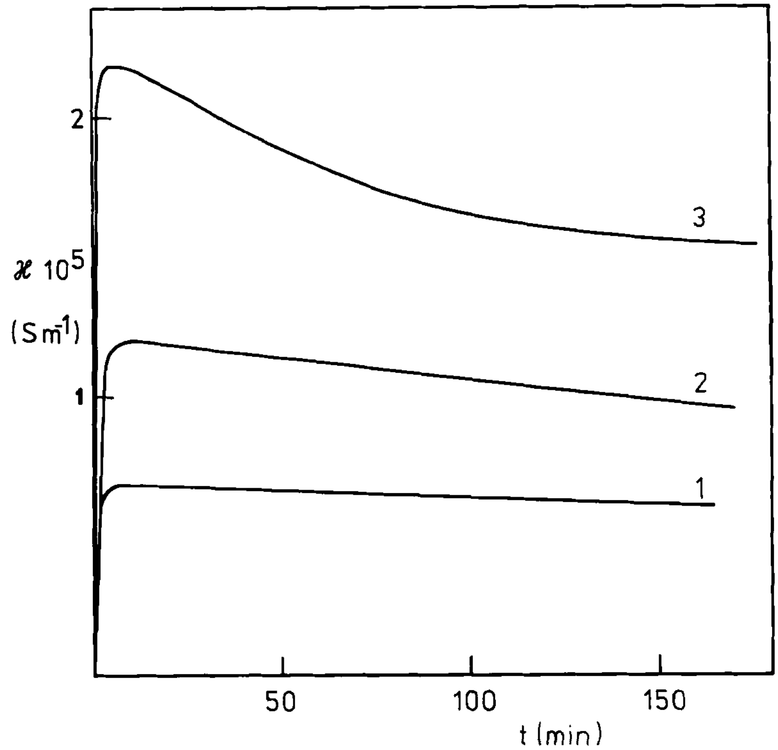
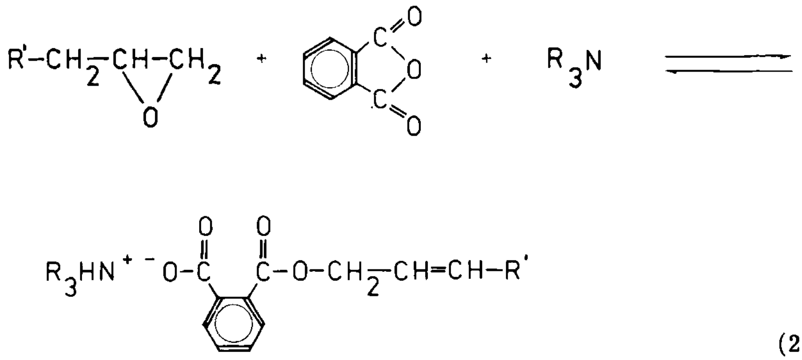


FIG. 4. Influence of the concentration of catalyst (CAB) on the course of conductivity curves of the copolymerization of HEPBP (0.5 mole/liter) with PA (0.5 mole/liter) in nitrobenzene at 120°C: (1) 0.00125 mole/liter; (2) 0.0025 mole/liter; (3) 0.005 mole/liter.

and subsequently, it settles at a value of 2.0×10^{-5} S/m (Fig. 3, curve 3). If nitrobenzene is used as a solvent and CAB (0.005 mole/liter) as a catalyst, the maximum conductivity of the polymerization system is attained very soon like in o-xylene, and subsequently, a decrease in conductivity is to be observed. Finally the conductivity reaches a constant value (1.5×10^{-5} S/m) (Fig. 4, curve 3). The maximum value of conductivity decreases with decreasing CAB concentration, but the subsequent decrease in conductivity becomes smaller (Fig. 4, curves 2 and 1). A decrease in concentration of the ammonium salt does not result in a proportional decrease in conductivity of the system.

DISCUSSION

The results of this study demonstrate that the process of copolymerization of epoxides with cyclic anhydrides involves an increase in conductivity of the polymerization solution, i. e., the formation of ionic particles which cause conductance. As to the catalysis by tertiary amine, it is obvious that a considerable increase in conductivity appears only in ternary systems where all three components of the polymerization system, i. e., epoxide, anhydride, and tertiary amine, are present and participate in the initiation of copolymerization, Eq. (2) [9].



(2)

The formation of ionic particles is in contradiction with the suggested effect of tertiary amines in the ternary transition complex [5] and gives evidence for an anionic mechanism of copolymerization. In contrast to the view of Fischer [2], the interaction between anhydride and tertiary amine is not sufficient for the formation of ionic particles, but, as is obvious from conductivity measurements, the ternary system epoxide-anhydride-tertiary amine is responsible for the formation of ionic active centers (Fig. 2). Similarly, the ternary system anhydride-tertiary amine-proton donor compound does not show increased conductivity either (Fig. 1), and the presence of epoxide is necessary again for a convenient conductivity to be attained. This fact contradicts the scheme of initiation of copolymerization modified by Tanaka and Kakiuchi [3] as well as the activation of tertiary amine by proton donor compound giving rise to ammonium base as suggested by Feltzin [4]. On the other hand, the presence of proton donor compound in the polymerization system shortens the time interval necessary to attaining the maximum conductivity (Fig. 2) which means, from the viewpoint of the copolymerization mechanism [9], a faster attainment of stationary concentration of ionic active centers and a reduction in the induction period of copolymerization. The time interval necessary to attain the maximum conductivity is consistent with the length of the induction period of copolymerization. The decrease in the time interval necessary to attain the maximum conductivity with increasing pK_a (cyclohexanol, BA) indicates the participation of proton donor compound in the initiation reaction; this is not a necessary condition, however, because the conductivity of the system increases even in the absence of proton donor compound.

From the viewpoint of polymerization mechanism [9] as well as constant concentration of tertiary amine in the polymerization system, a decrease in conductivity in the subsequent stage of reaction, as observed in the solution of o-xylene and chlorobenzene, is remarkable. If the copolymerization is carried out in a solution of 1,1,2,2-tetrachloroethane and nitrobenzene, such decrease in conductivity does not appear and the conductivity remains at a constant value. This effect is most likely due to the increase in molecular weight during copolymerization as well as to the quality of solvent with respect to the solubility of the arising copolymer. The increase in molecular weight due to the prolongation of copolymerization time was ascertained experimentally by Tanaka and Haung [10]. It is clear that the mobility of macroions decreases with increasing molecular weight and viscosity of the system which is reflected in the decrease in conductivity.

The type of solvent influences the conductivity of polymerization solution. Because of the polar character of monomers and polymer, the solvation of macromolecules also increases with increasing polarity of the solvent. The polymer formed is less soluble in poorly polar solvents such as o-xylene and chlorobenzene and precipitates to some extent even on slight cooling. Owing to strong solvation in polar 1,1,2,2-tetrachloroethane and nitrobenzene, the cooling of solution does not bring about the precipitation of polymer from the reaction system even in advanced stages of polymerization. The solvation effect also causes a different degree of dissociation of the ion pairs. Thus, the absolute value of conductivity of the copolymerization solutions also increases with polarity of the solvent (Figs. 2 and 3). The comparison of the maximum conductivities with the values of rate constants of the copolymerization, which is a first-order reaction with respect to the concentration of epoxide or anhydride, shows that there is no correlation between these data (Table 1). It follows that the copolymerization of epoxides with anhydrides is catalyzed by the active centers in both dissociated and nondissociated form.

In the copolymerization of epoxide with anhydride catalyzed by alkali salt (BzK), the initial increase in conductivity is affected by the process of dissolution and dissociation of the salt in the

TABLE 1. Maximum Values of Conductivity and Rate Constants of the Copolymerization of HEPBP (0.5 mole/liter) with PA (0.5 mole/liter) Catalyzed by THAm (0.025 mole/liter) at 120° C in Various Solvents

Solvent	κ_{max} (S/m)	$k \times 10^5$ (sec^{-1})[a]
o-Xylene	9.4×10^{-8}	6.5
Chlorobenzene	5.1×10^{-7}	6.4
Nitrobenzene	2.0×10^{-5} (1.5×10^{-5})[b]	20.4

[a] Data of Luston et al. [9].

[b] Value at the inflection point in the conductivity curve.

polymerization solution. After the rapid increase in conductivity in the first stage of copolymerization, the subsequent increase in conductivity may be attributed to the change of the type of anion in propagation reactions of the copolymerization which obeys the scheme put forward by Schwenk [1]. The instantaneous increase in conductivity (Figs. 2 and 4) observed in the copolymerization of epoxide with anhydride catalyzed by ammonium salt in o-xylene or nitrobenzene is evidence that the catalyst dissociates after dissolving in the system. The degree of dissociation depends on the polarity of solvent as well as on the concentration of ammonium salt in solution (Fig. 4). The degree of dissociation increases with increasing polarity of the solution and decreasing concentration of the salt. The decrease in conductivity of the polymerization solution may be interpreted, as in case of the copolymerization catalyzed by tertiary amine, as a consequence of the mobility of macroions and of the solvent effect. Similarly, the difference between the maximum conductivities in o-xylene and nitrobenzene may be interpreted on the basis of the solvation effect of solvent and varying degree of dissociation in solvents with different polarities.

By comparing the conductivities of polymerization solutions with different catalysts in equal solvent, it may be stated that conductivity decreases in the order ammonium salt > alkali salt > tertiary amine (either in the presence or in the absence of proton donor compound). The time interval necessary for attaining the maximum conductivities also decreases in the above order. Therefore, if tertiary amine is catalytically effective in consecutive reactions yielding the active centers of the ammonium type [9] and salts are operative in the form of ion pairs or dissociated form, these differences may be attributed to the differences in character of anion and cation as well as to a lower concentration of the proper active centers which are products of equilibrium reactions in case of the catalysis by tertiary amines.

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