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Amino-quinoid Polymeric System. The Preparation of a Polyester Containing 2,5-Diamino-*p*-benzoquinone Nuclei and Its Crosslinking

Ju KUMANOTANI, Kazuyuki SUGITA,[*1] Seiji KAZAMA[*2] and Toshio YOSHIKAWA[*3]

The Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo

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A polyester containing 2,5-diamino-*p*-benzoquinone nuclei was prepared by the polycondensation of 2,5-bis(ω-carboxyl-pentylamino)-*p*-benzoquinone with polyethylene glycol 400 at 160°C, 170°C and 180°C. At 160°C the esterification was brought about easily without gelation, giving an amino-quinoid polyester (prepolymer), but above 170°C an unexpected gelation was observed. The amino-quinone nuclei incorporated in the polyester thus prepared were confirmed by NMR spectroscopy. To make clear the influence of the amino-quinone nuclei upon the gelation, the thermal reactions of the model compounds, the above amino-quinoid dibasic acid, and its ethyl ester were investigated by means of IR spectroscopy and chemical analysis. It was concluded that the hydrogen atoms in the amino-groups of the quinone move to the oxygen atoms and that the resulting hydroxy groups combine with each other to form an ether bond as a result of dehydration. When the prepolymer prepared at 160°C was heated at 170°C for 4 hr with *p*-toluenesulfonic acid (5% by weight) or at 180°C for 8 hr without the acid catalyst, there was obtained an infusible and insoluble film which made crosslinkage as shown in the above mechanism.

While studying a new type of crosslinking polyamides, the present authors found that there is a possibility that the 2,5-diamino-*p*-benzoquinone nuclei introduced in the linear polymer chains will become new functional groups to undergo a crosslinking reaction upon the application of heat. Therefore, in order to elucidate the contribution of the amino-quinone nuclei linked in the polymer backbone to the crosslinking reaction, the present paper will deal with the system of a polyester prepared from 2,5-bis(ω-carboxyl-pentylamino)-*p*-benzoquinone (designated as Q-ACA) and a polyethyleneglycol. In comparison with the polyamide system, a clear interpretation can be obtained IR-spectroscopically for the change in the amino-quinone nucleus without any overlapping of its characteristic absorption bands (see Table 1) with those of the polyamides.

Thus, by using Q-ACA and a commercially-available polyethyleneglycol, PEG 400, we attempted to prepare a linear amino-quinoid polyester without gelation. The progress of the esterification was interpreted in terms of the results of the chemical and IR-spectral analyses. We also tried to reveal the mode of the crosslinking of the amino-quinone nucleus introduced into the polyester by investigating the spectral change in the amino-quinone nucleus, using model compounds of Q-ACA and its ethyl ester. The variation in the linkage of the resulting polyester was also accommodated by the mechanism shown in the scheme. (Eqs. (1), (2), and (3))

Experimental

Materials. PEG 400 of a chemically-pure grade was obtained commercially.

2,5-Bis(ω-carboxyl-pentylamino)-*p*-benzoquinone (Q-ACA) was prepared by the reaction of *p*-benzoquinone with ω-aminocaproic acid according to the method used for the preparation of 2,5-dialkylamino-*p*-benzoquinone derivatives,[1)] except that methanol was used as the solvent instead of ethanol. Methanol gave a product with a higher purity than did ethanol. The blowing of air into the reacting solution, with or without cuprous acetate,[2)] had no effect upon the yield. An example of the preparation of Q-ACA is the following: a solution of amino-caproic acid (12.9 g, 0.10mol) in 550 m*l* of methanol was mixed with a solution of *p*-benzoquinone (16.2 g, 0.15mol) in 200 m*l* of methanol in a one-liter, round-bottomed flask equipped with a refluxing condenser, and then the mixture was refluxed in a boiling

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[*1] Present address: Department of Graphic Engineering, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba City.

[*2] Present address: Technological Research Laboratories, Takeda Chemical Industries, Osaka.

[*3] Present address: Ube Central Research Laboratories, Ube Industries, Ltd., Oguchi, Ube City.

1) a) see, *e. g.*, L. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York (1961), p. 853. b) O. Suchanek, *J. Prakt. Chem.*, **90**, 479 (1914). c) M. Martynoff and G. Tsatsas, *Bull. Soc. Chim. France*, **1947**, 52.

2) R. Baltzly and E. Lorz, *J. Am. Chem. Soc.*, **70**, 123 (1948); A. H. Crosby and R. E. Lutz, *ibid.*, **78**, 1233 (1956).

water bath for 15 min; the resulting solution was cooled to room temperature with ice. The brownish precipitates thus formed were filtered off, washed with benzene, dried *in vacuo*, and found to weigh 12.9 g (theor. 71.3%); decomposing melting point, *ca.* 204°C (measured by the capillary method).

Found: C, 58.75; H, 7.06; N, 7.49%. Calcd for $C_{18}H_{26}O_6N_2$: C, 59.00; H, 7.16; N, 7.65%.

The infrared spectrum of this compound was consistent with that of Q-ACA (see Table 1).

2, 5-Bis (ω-ethoxycarbonyl-pentylamino)-*p*-benzoquinone (designated as Q-ACEt hereafter) was prepared by the reaction of *p*-benzoquinone with the ω-aminocaproic acid ethyl ester much as in the case of Q-ACA; a solution of the ω-aminocaproic acid ethyl ester (12.7 g, 0.08mol) in 50 m*l* of methanol was reacted with a solution of *p*-benzoquinone (13.0 g, 0.12mol) in 200 m*l* of methanol, and the resulting yellowish red precipitates were recrystallized from chloroform, dried *in vacuo*, and found to weigh 5.0 g (theor. 29.6%); mp 103—104°C.

Found: C, 62.40; H, 8.25; N, 6.77%. Calcd for $C_{22}H_{34}O_6N_2$: C, 62.54; H, 8.11; N, 6.63%.

The infrared spectrum of this compound was consistent with that of Q-ACEt (compare Fig. 5).

Polyesterification of Q-ACA with PEG 400. In a 50-m*l* flask equipped with an air-tight stirrer, a nitrogen inlet tube reaching to the bottom of the flask, a thermometer, and a short air-condenser for collecting water formed during the reaction, there was placed an equimolar mixture of Q-ACA (3.66 g, 0.01mol) and PEG 400 (4.00 g, 0.01mol). The mixture was heated while being stirred at 160°C, 170°C, or 180°C by means of an oil bath, while a slow stream of deoxygenated nitrogen was passed through it. In order to measure the degree of polyesterification, a sample (0.1—0.5 g) was taken out from the reacting mixture every two or three hours. This sample was dissolved in 50 m*l* of a mixed solvent (acetone-methanol-water, 10 : 5 : 1 by volume) and titrated with a 0.1N KOH ethanol solution on a Potentiograph, E336 (Methrohm Co., Ltd.). The change in the acid value *vs.* the reaction time is shown in Fig. 1.

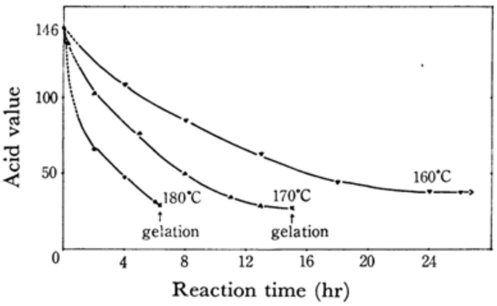

Fig. 1. Relation of the acid-value *vs.* reaction time in the polyesterification of Q-ACA with PEG 400.

Measurement of Curability of the Prepolymer. An acetone-methanol (2 : 1 by volume) solution of the prepolymer was evaporated on a glass plate (1 × 10 × 30 mm) at room temperature with or without the addition of 5% of *p*-toluenesulfonic acid as a catalyst. The thin film thus formed on the glass plate was placed into a heating apparatus *in vacuo*. In order to estimate the extent of the crosslinking of the film, the specimen on the glass plate was dipped in a mixed solvent of acetone-methanol (2 : 1 by volume) at room temperature for ten days or more to determine its solubility; the glass transition temperature was measured by the swinging-beam method.[3]

Results and Discussion

Polyesterification of Q-ACA with PEG 400. *Gelation.* On the basis of the relation between the acid value and the reaction time (see Fig. 1), the esterification of Q-ACA with PEG 400 was found to progress at 160°C, 170°C, and 180°C. In the polyesterification carried out above 170°C, gelation was found unexpectedly; it may be due to the amino-quinone nuclei, since such gelation cannot be seen in the usual polyesterification of a diol with a dibasic acid. The observed gelation time

Table 1. Characteristic absorption bands of 2,5-diamino-*p*-benzoquinone nucleus

Wave number (cm^{-1})	Assignment
3270 (s.)	νN–H
1635 (m.)	νC=C
1550 (s.)	νC=O
1500 (s.)	Amide II type band
1460 (s.)	δC–H (in plane)

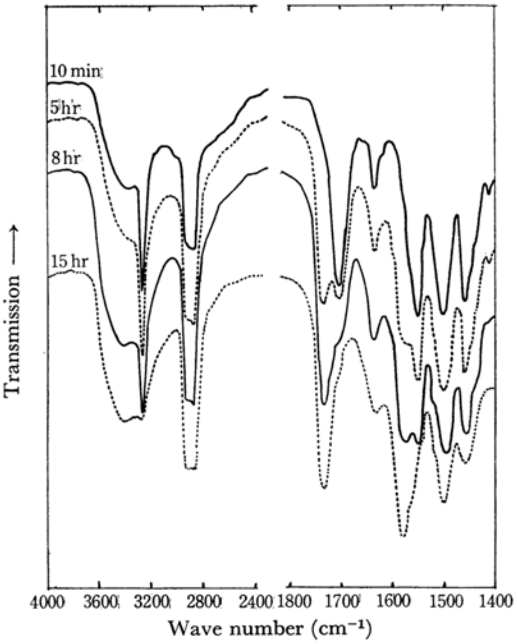

Fig. 2. IR-spectral change *vs.* reaction time in the polyesterification of Q-ACA with PEG 400 at 170°C (KBr disk).

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[3] K. Sato, H. Kiryu and Y. Inoue, *J. Japan Soc. Colour Material*, **31**, 81 (1958).

(the interval between the beginning of the heating of the reaction mixture and the gleation) was 15 hr at 170°C and 6.3 hr at 180°C. Accordingly, any polyesterification without such gelation should be carried out at 160°C or below.

Infrared Spectral Change. Upon an examination of the spectral change observed during the course of the polyesterification of Q-ACA with PEG 400, the characteristic absorption bands of Q-ACA could be assigned as is shown in Table 1.[4]

As may be seen from the spectral change *vs.* the reaction time (see Fig. 2), as the polyesterification progresses, an increase in the absorption at 1730 cm^{-1} (characteristic of the carbonyl group of the ester) and a decrease in the absorption at 1705 cm^{-1} (characteristic of the carbonyl group of the carboxylic acid) may be seen.

Furthermore, remarkable spectral changes were observed for the characteristic absorption bands of the amino-quinone nucleus during the polyesterification. For example, in the polyesterification at 160°C, shown in Fig. 2, characteristic bands of the amino-quinone nucleus at 3270, 1500, and 1460 cm^{-1} decrease and the absorption band at 1550 cm^{-1} shifts to 1580 cm^{-1} as the esterification progresses. These spectral changes, nevertheless, cannot be interpreted in terms of the chemical change of the amino-quinone nucleus.

An infrared spectrum of the solution of an amino-quinoid compound differs markedly from that of a solute (*e. g.*, in a KBr disk) as a result of the strong molecular interaction of solid solute;[4] the same is true of 2,5-bis(*n*-butylamino)-*p*-benzoquinone, as is shown in Fig. 3. This spectral difference observed for the amino-quinoid compound was used for the interpretation of the spectral change already observed in the above polyesterification. At the initial stage of the reaction, the reacting mixture, because the solubility of Q-ACA in PEG 400 was small, showed absorption bands characteristic of the solid amino-quinone, but as the esterification progressed and as the homogeneity of the reacting mixture increased, the absorptions characteristic of the amino-quinone dissolved in a solvent appeared. Moreover, the fact that the absorption shifts from 1550 cm^{-1} to 1580 cm^{-1} is in harmony with the above spectral results.

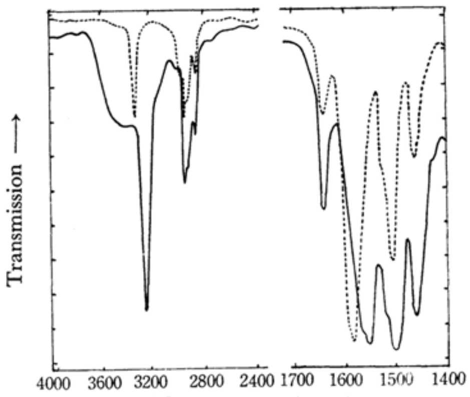

Fig. 3. IR-spectra of 2,5-bis(*n*-butylamino)-*p*-benzoquinone (—, KBr disk; ---, $\mathrm{CHCl_3}$ solution).

NMR Spectra. A further chemical evidence for the stability of the amino-quinone nucleus was given by the NMR spectrum, measured for the polyester prepared at 160°C for 26 hr; the peak ratio between the proton (τ, 2.29) attached to nitrogen and the proton (τ, 4.81) attached to the quinone nucleus was approximately 1 : 1. Their peak intensities were comparable to the expected

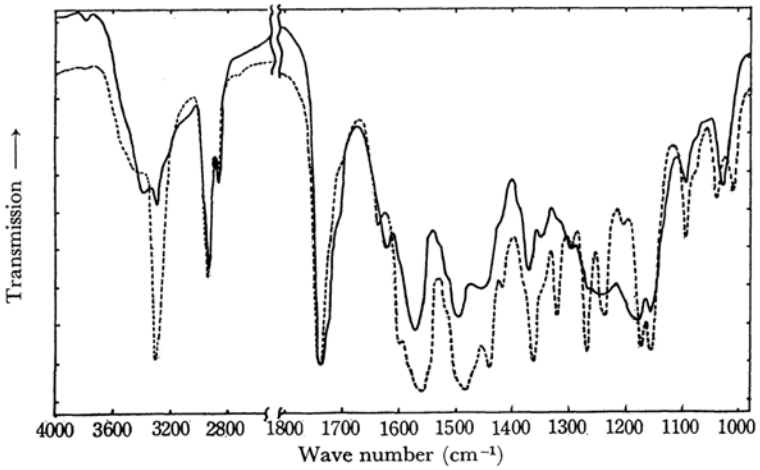

Fig. 4. IR-spectral change of Q-ACEt (---), kept at 200°C for 8 hr (—), (KBr disk).

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[4] Unpublished data: the spectral data of the amino-quinoid compounds will be shortly submitted for publication.

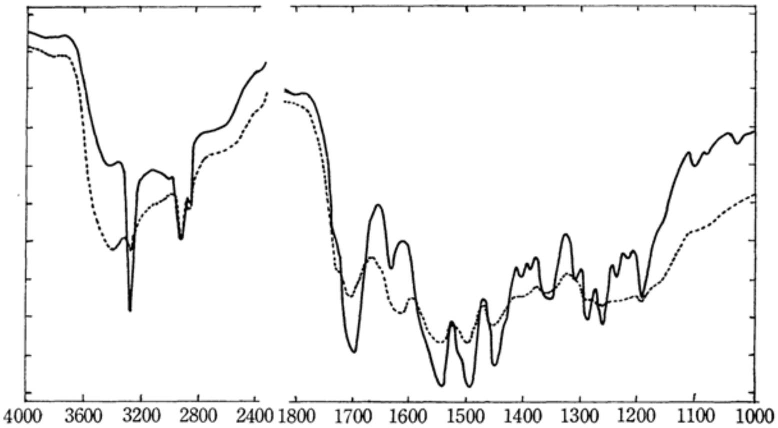

Fig. 5. IR-spectral change for Q-ACA kept at 170°C for 4 hr (—) and at 170°C for 8 hr (---), (KBr disk).

amount of the amino-quinone nuclei involved in the polyester. The assignment of the signals of protons attached to both nitrogen and the quinone nucleus was made using Q-ACEt as a standard material.

On the basis of the above results, it can readily be concluded that the polyester prepared by the reaction of Q-ACA with PEG 400 at 160°C has the expected amino-quinone nuclei.

Crosslinking Character of the 2,5-Diamino-quinone Nucleus. To avoid the trouble of interpreting the infrared spectra recorded during the course of the polyesterification, model compounds, *i. e.*, Q-ACEt and Q-ACA, were used to interpret the mode of the crosslinking of the polyesters containing amino-quinone nuclei in terms of their infrared spectra; a sample (50 mg), placed in an evacuated ampoule, was kept between 150°C and 210°C (±1°C) in an oil bath, and the spectral changes were observed in a KBr disk.

Q-ACEt. When the amino-quinone was kept at 190°C for 8 hr, the change (2—3%) of the amino-quinone was found IR-spectroscopically in a chloroform solution by measuring the intensity of the band at 3270 cm^{-1} (νN–H). As may be seen in Fig. 4, an abrupt decrease in the absorption was observed in the amino-quinone kept at 200°C for 8 hr. With this spectral change, the following absorption bands appeared: the broadened band at 3000—3600 cm^{-1}, attributable to the hydroxy groups formed according to Eq. (1); the band at 1625 cm^{-1}, attributable to the C=C group of the quinonediimine formed (Eq. (1)); the bands near 1250 cm^{-1} and 1027 cm^{-1}, attributable to the ether group of the compound formed due to Eq. (2), and understandable considering that vinyl ether homologues show the characteristic absorption bands of the ether group at 1270—1210 cm^{-1} and 1075—1020 cm^{-1} 5) and that the compound under consideration has structual units similar to those of vinyl ether compounds.

From the above spectral observations, it may be seen that hydrogen atoms in the amino-groups of the amino-quinone move to the oxygen atoms and that the resulting hydroxy groups combine with each other as a result of dehydration to form ether bonds (Eqs. (1), (2) and (3)).

Q-ACA. The amino-quinone kept at 170°C for 4 hr showed no apparent spectral change, but that kept for 8 hr showed a clear change in its nucleus. As is shown in Fig. 5:

(1) The absorption bands characteristic of the amino-quinone nucleus show a minor decrease in its intensity.

(2) The increased, broadened band at 3000—

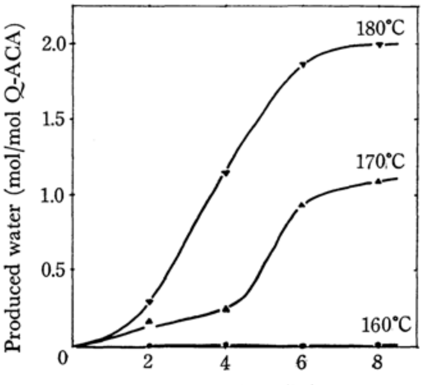

Fig. 6. The amount of water produced in heating Q-ACA at various temperatures.

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5) see, *e. g.*, M. Ōki, "Sekigai Kyushu Supekutoru," (The Infrared Spectra), The Tokyo University Press, Tokyo (1968), p. 193.

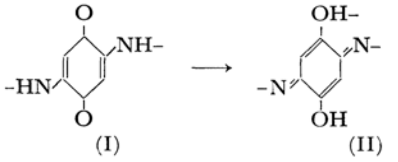
3600 cm^{-1} is attributable to the hydroxy groups formed according to Eq. (1).

(3) The band attributable to the carbonyl group of the ester group occurs at 1730 cm^{-1} as a shoulder, while the absorption band of the carbonyl group at 1705 cm^{-1} decreases. This may be due to the ester group formed by the reaction between the carboxylic group present in the starting dibasic acid and the hydroxy group formed as has already been demonstrated (Eqs. (2) and (3)).

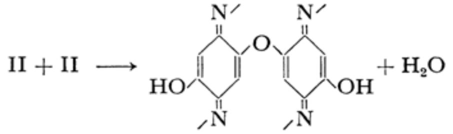
(4) In the region from 1100 cm^{-1} to 1300 cm^{-1}, near 1230 cm^{-1} and 1155 cm^{-1} there appear broadened absorption bands which may be ascribed to the ether (Eq. (2)) and ester (Eq. (3)) groups respectively. This assignment is reasonable in view of the spectral results shown already for the thermal reaction of Q-ACEt.

Further evidence supporting Eqs. (1), (2) and (3) was obtained by measuring the amount of the water formed in the thermal reaction of Q-ACA by the Karl-Fisher method: Samples (100 mg) were placed in evacuated ampoules. Several ampoules thus prepared were kept at 160°C, 170°C, or 180°C in an oil bath, and then each ampoule was taken out from the bath at intervals and cooled. The reacting mixture was taken out from the opened ampoule with 10 m*l* of methanol and submitted to titration. In order to calibrate the amount of the water formed, a blank test was carried out with the same volume of methanol as was used in the determination. The relation between the amount of the water formed and the time is plotted in Fig. 6. Figure 6 demonstrates that at 160°C and 8 hr heating, no formation of water was observed, and the amount of water per mole of Q-ACA was approximately 1 and 2 mol at 170°C-8 hr and 180°C-8 hr heating respectively, indicating that the amino-quinone nucleus was changed thermally above 170°C and that the esterification reaction (Eq. (3)) between the carboxyl groups of Q-ACA and the hydroxyl groups formed contributes predominantly to the formation of the water at 180°C.

On the basis of the results of the IR-spectral observation of the thermal reaction of Q-ACA and Q-ACEt, together with those of the above dehydration reaction of Q-ACA, the following scheme can be proposed for the thermal reaction of the 2,5-diamino-quinone nucleus; this scheme involves the isomerization of the amino-quinone nucleus and subsequent reactions:

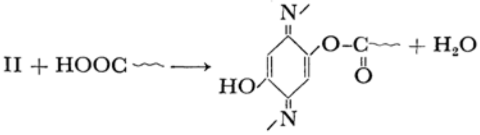


(1)



(2)

In addition, in the case of Q-ACA:



(3)

Crosslinking Character of the Quinoid Prepolymer. The mode of the crosslinkage of the prepolymer prepared by the reaction of Q-ACA with PEG 400 at 160°C for 26 hr was examined for a film baked at 180°C for 8 hr, and for that made by the addition of *p*-toluenesulfonic acid (5% by weight) to it, followed by baking at 170°C for 4 hr. For this purpose, the glass transition temperature on the cured film was measured by the swinging-beam method or the solubility of the film in a mixed

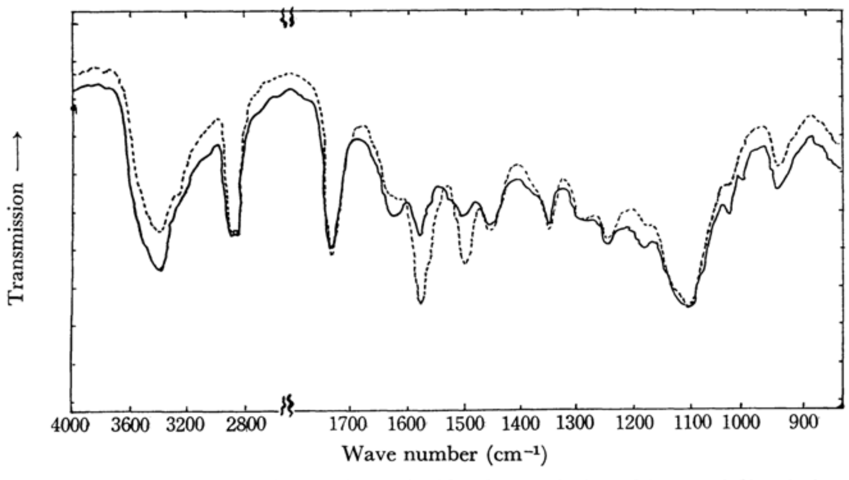


Fig. 7. IR spectra of an amino-quinoid polyester (---) and its cured film (—) at 170°C-4 hr heating with *p*-toluenesulfonic acid (5% by weight).

solvent of acetone-methanol (2 : 1 by volume) was determined. The reaction that occurred during the curing was inferred by means of an IR-spectral analysis of the cured film (see Fig. 7).

The glass-transition temperature was below 20°C for the film baked at 180°C-8 hr and 30°C for that baked at 170°C-4 hr. These facts show that the acid-catalyzed effect is predominant in giving an insoluble and infusible film, and that the glass-transition temperatures found on the cured films were not as high as had been expected from the rigid structure of the amino-quinone nucleus. This may be ascribed to the existence of flexible polyethylene ether chains introduced into the polymer chain by the PEG 400.

As may be seen in Fig. 7, a decrease in the absorption band characteristic of the amino-quinone nucleus and the appearance of the bands at 1250 cm^{-1} and 1030 cm^{-1} characteristic of the ether bond were more obvious in the film baked in the presence of *p*-toluenesulfonic acid than in that of the original polyester (prepolymer).

The thermal and acid-catalyzed baking procedures which bring about the crosslinkages to form an insoluble and infusible film are almost quite the same, since the spectra observed on the baked films formed by these two different methods are almost the same.

These results obviously indicate the contribution of the amino-quinone nuclei incorporated in the polyester to the crosslinking reaction through the steps of Eqs. (1), (2) and (3).

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