# Study of Crosslinking Acid Copolymer/DGEBA Systems by FTIR

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**ABSTRACT:** A study of crosslinking of diglycidylether of bisphenol A (DGEBA) by four copolymers of poly(acrylic acid-*co*-styrene) having different acid group percentages, in the range 7.6–76.6%, was done by FTIR. The study was done in the isothermal mode for four different temperatures, the reaction being accelerated by triethylamine. We followed each by temperature and the variation of the area of the epoxy infrared band (912–916 cm$^{-1}$) versus time. The results showed that the mechanism was complex and depended on the acid composition in the copolymer. Three types of reaction were involved: addition esterification, etherification, and condensation esterification. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2033–2051, 2003

**Key words:** diglycidylether of bisphenol A; poly(acrylic acid-*co*-styrene); curing; FTIR; crosslinking

## INTRODUCTION

Properties of thermoset resins depend on their degree of crosslinking. Comprehension of the curing mechanism is essential to understand the relationship of structure to properties. It is therefore of interest to follow and observe the chemical changes that take place during the crosslinking reaction.

FTIR spectroscopy is suitable[1,2] for following the variations occurring in such a material when it is submitted to a curing process[3–10] to completion.

The present work deals with crosslinking of the acid copolymer/diglycidylether of bisphenol A (DGEBA) system as followed by FTIR. Four copolymers at different compositions in poly(acrylic acid-*co*-styrene) were made. The accelerator used was the tertiary amine triethylamine.

The curing kinetics of the same systems were studied in previous work using the DSC method in two modes (isothermal and nonisothermal).[11,12] An appropriate kinetic model was applied in each case to calculate the kinetics parameters.

## EXPERIMENTAL

### Instruments

IR spectra were obtained through use of a Nicolet 710 FTIR (Nicolet Analytical Instruments, Madison, WI).

Sixty coadded interferograms were scanned at 2 cm$^{-1}$ of resolution. Functions of the optical bench were entirely automated and both the acquisition and the processing of the signal were made with the data-processing software Advantage. A thermostated cell (ACCUSPEC Model 20), a digital temperature controller, and a linear temperature programmer (type ACCUSPEC) were used jointly for the isothermal programming.

### Materials

DGEBA was used (DER 332; commercially available from Dow Chemical Co., Midland, MI) with an equivalent epoxy of 174 g. Four copolymers of poly(acrylic acid-*co*-styrene) at various compositions in acrylic acid were synthesized by free-radical polymerization with azobisisobutyronitrile (AIBN) as initiator and dioxan as solvent, at a temperature of 70°C and reaction time of 7 h. The compositions made are summarized in Table I. The copolymers were precipitated in hexane, purified, and dried under vacuum. Their compositions were determined by UV spectroscopy at 250 nm (absorption of styrene moieties). Table II shows the compositions of these copolymers. Triethylamine (TEA) was used as accelerator. For each given system of copolymer/DGEBA, we fixed the ratio (*r*) = acid function/epoxy equivalent, according to the results of the nonisothermal DSC study.[11] Table III reports the different results of *r*.

### Preparation of samples

The copolymer and DGEBA were mixed in 2 mL of tetrahydrofuran (THF) and stirred until homogeniza-

**TABLE I**
**Conditions for Synthesis Copolymers**

| Copolymer reference | Acrylic acid (g) | Styrene (g) | AIBN (g) |
|---|---|---|---|
| SAA1 | 6.3 | 48.6 | 0.055 |
| SAA3 | 10.5 | 27.0 | 0.037 |
| SAA5 | 31.5 | 9.0 | 0.040 |
| SAA6 | 48.6 | 6.3 | 0.055 |

tion and then the TEA (at a percentage of 15% TEA–epoxy) was added to the solution. The solution was deposited on a Teflon plate in the form of a thin film and degassed in a vacuum oven at room temperature, after which the sample was placed in the thermostated cell.

FTIR purging was undertaken by nitrogen before each test. IR spectra of each pure used reactant, TEA, DGEBA, SAA1, SAA3, SAA5, and SAA6 were taken first.

The kinetic study of each system was performed at four isothermal temperatures[12]:

1. SAA1/DGEBA: $T$ = 110, 105, 100, and 95°C
2. SAA3/DGEBA: $T$ = 90, 85, 80, and 75°C
3. SAA5/DGEBA: $T$ = 100, 95, 90, and 85°C
4. SAA6/DGEBA: $T$ = 95, 90, 85, and 80°C

Each cured system was postcured at 100°C for 96 h.

## RESULTS AND DISCUSSION

IR spectra of TEA, DGEBA, and SAA1 are represented, respectively, in Figures 1–3. Tables IV–VI give corresponding positions of the absorption bands.[13–15] As an example, we represent the spectrum of SAA3 in Figure 4 and Table VII gives the positions of the absorption bands.

Figures 5–8 represent, respectively, spectra at room temperature of the four systems: SAA1/DGEBA, SAA3/DGEBA, SAA5/DGEBA, and SAA6/DGEBA.

Table VIII gives the position of absorption bands of the SAA1/DGEBA system; the three other systems have similar absorption bands. Table IX reports the position of absorption bands of SAA3/DGEBA.

**TABLE II**
**Composition in Acrylic Acid Moieties of the Copolymers**

| Copolymer reference | Composition in acrylic acid moieties (wt %) |
|---|---|
| SAA1 | 7.6 |
| SAA3 | 29.5 |
| SAA5 | 63.2 |
| SAA6 | 79.6 |

**TABLE III**
**Results of $r$ for Each System SAAx/DGEBA**

| System | $r$ |
|---|---|
| SAA1/DGEBA | 0.7 |
| SAA3/DGEBA | 0.7 |
| SAA5/DGEBA | 1 |
| SAA6/DGEBA | 1 |

Figures 9–12 represent for three reaction times ($t$ = 0, 60, and 150 mn), the spectra of

1. SAA1/DGEBA: $T$ = 110°C
2. SAA3/DGEBA: $T$ = 90°C
3. SAA5/DGEBA: $T$ = 100°C
4. SAA6/DGEBA: $T$ = 95°C

In the same figures the corresponding postcured systems at 100°C for 96 h are represented.

Our study deals with the reactivity of epoxy groups vis-à-vis carboxy groups. The variation of the peak area of epoxy group absorption at 916 cm$^{-1}$ allows one to follow the evolution of the reaction as a function of time. This variation is quantified by considering the aromatic band as the internal standard (stretching vibration of the bond C=C at 1454 cm$^{-1}$). The epoxy fractional conversion is calculated as follows:

$$\alpha = 1 - \frac{(A_{\text{epoxy}}/A_{\text{aromatic}})_t}{(A_{\text{epoxy}}/A_{\text{aromatic}})_{t=0}}$$

where $A_{\text{epoxy}}$ is the area of epoxy group's absorption and $A_{\text{aromatic}}$ is the area of aromatic absorption.

## DISCUSSION

### System SAA1/DGEBA

The decrease of the intensity of the characteristic band of epoxy at 912 cm$^{-1}$, the increase of the intensity of the characteristic band of esters at 1184–1156 cm$^{-1}$, and the increase of band at 3600–2400 cm$^{-1}$ characteristic of the hydroxyls, which were observed during the reaction (150 min), indicate that addition esterification reaction occurred.

The three groups, epoxy, carboxy, and ester, all absorb in the same region at 1250–1230 cm$^{-1}$, corresponding in each case to the stretching vibration of a C—O bond. The decrease of the intensity band is attributed to the consumption of epoxy and carboxy groups, and the increase of intensity is attributed to the formation of ester groups. These variations explain the change observed in this zone during the cure reaction.
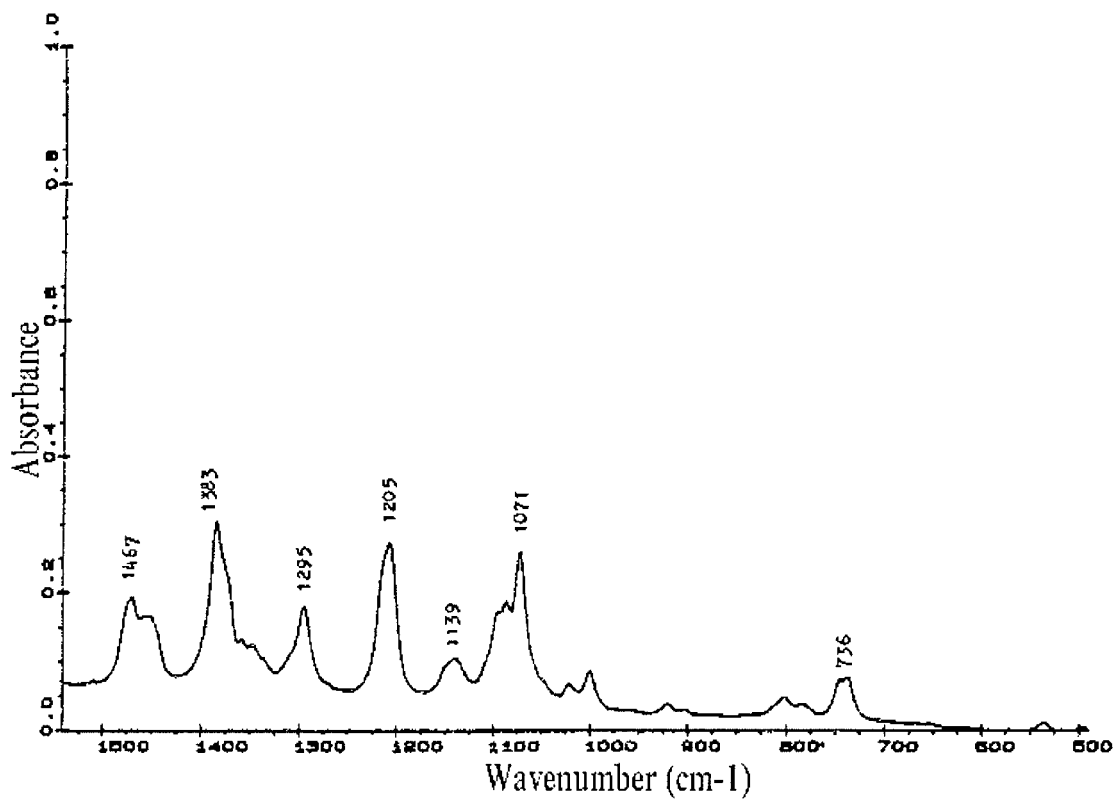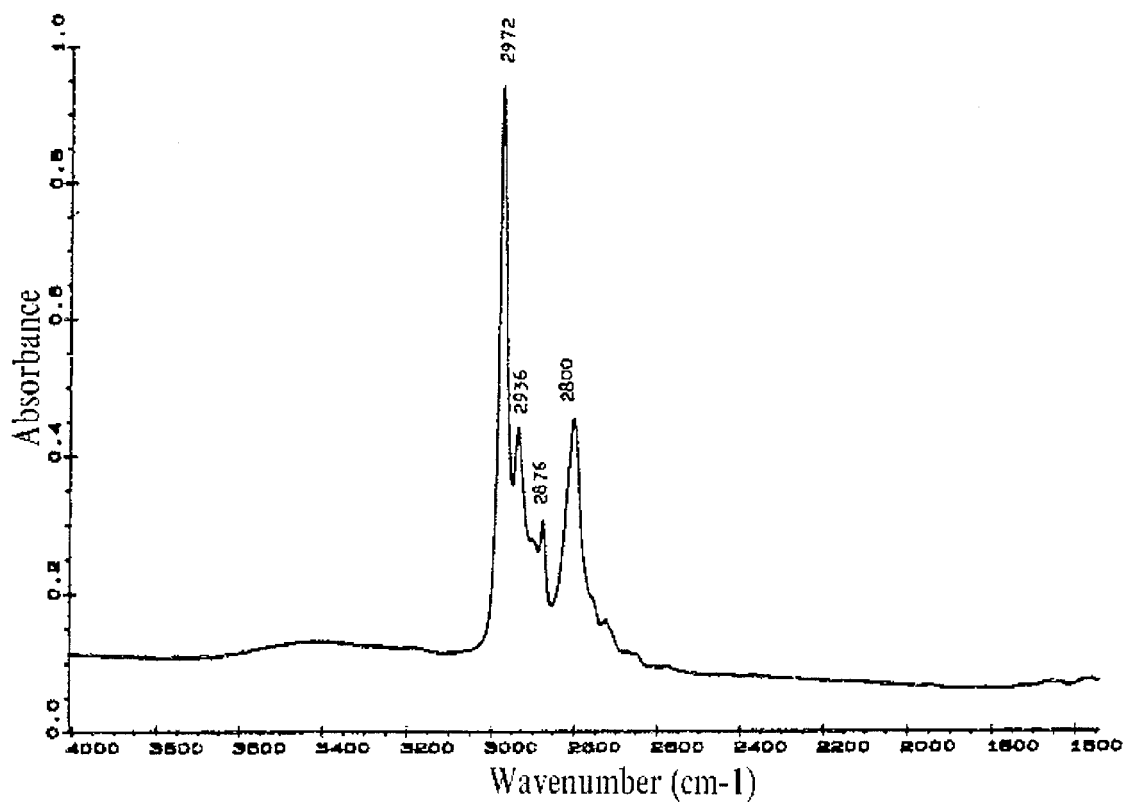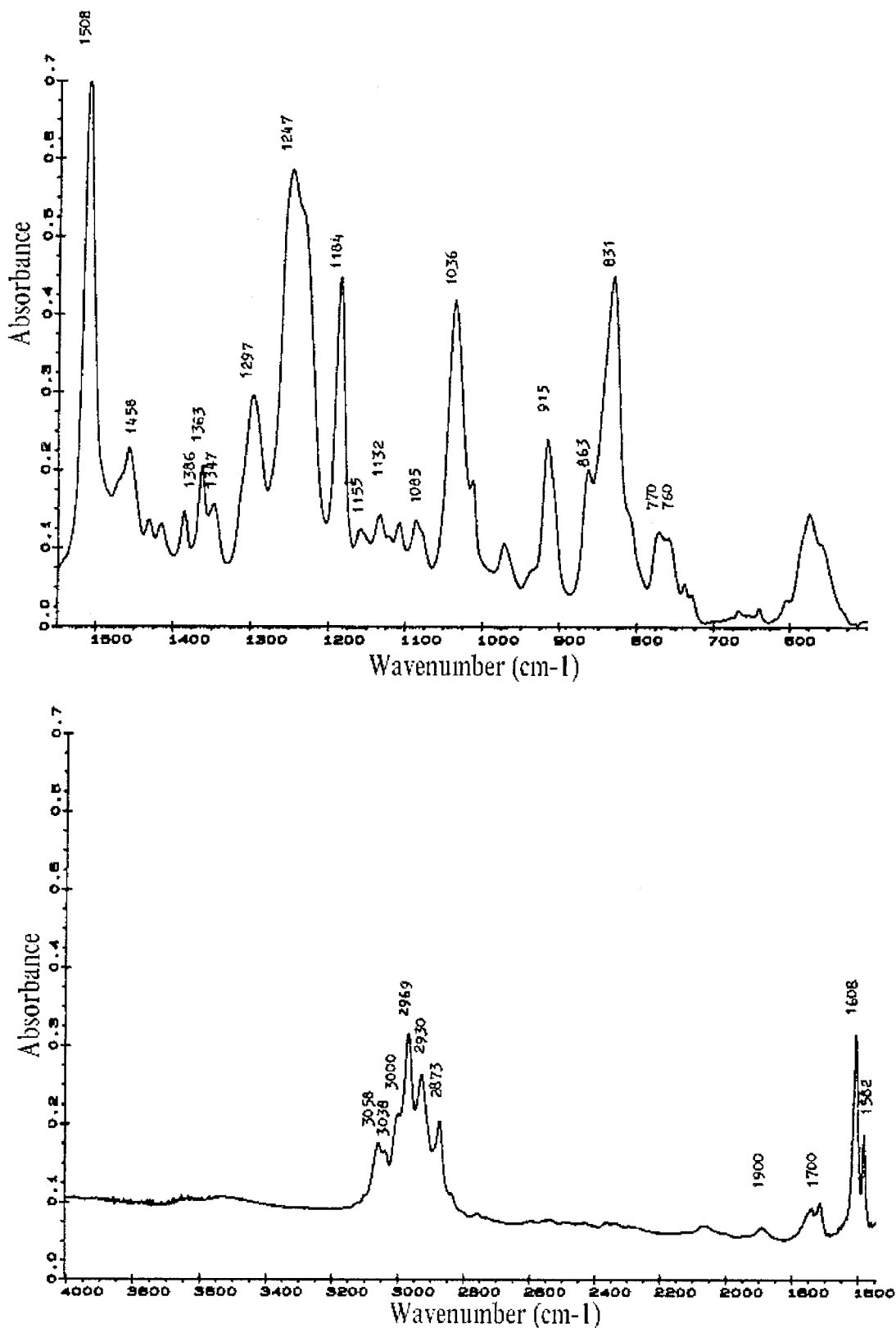
**Figure 1**  FTIR spectrum of TEA.
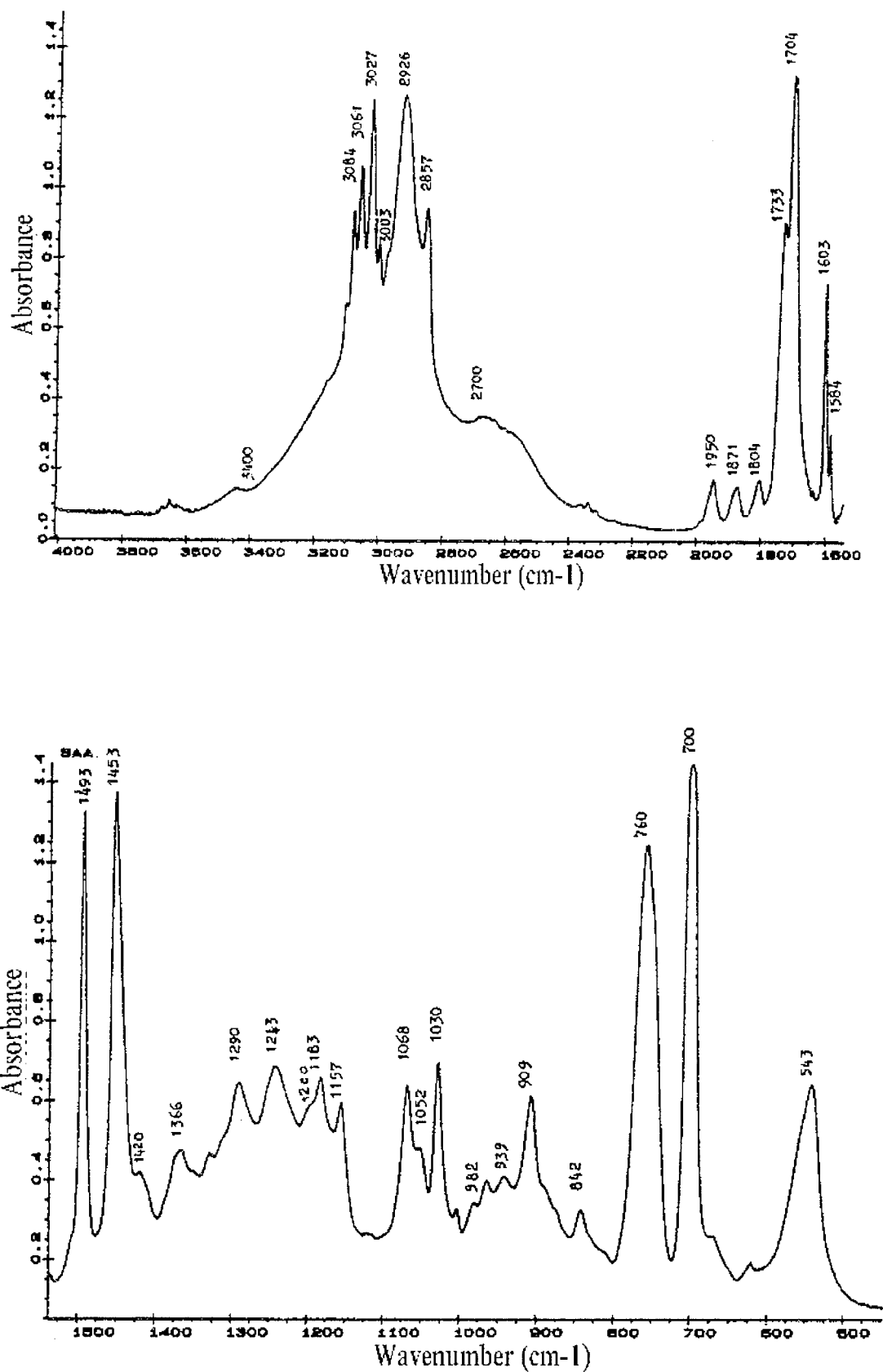
**Figure 2** FTIR spectrum of DGEBA resin.

**Figure 3** FTIR spectrum of the SAA1 copolymer.

## TABLE IV
### Attribution of Frequency Bands of TEA

| Wavenumber (cm$^{-1}$) | Attribution[a] |
|---|---|
| 736 | $\gamma CH_{2\ r}$ (rocking) |
| 1071 | $\nu C—N$ |
| 1205 | $\gamma CH_{3\ r}$ (methyrocking) |
| 1293 | $\gamma CH_{2\ t} + \gamma CH_{2\ w}$ (twisting and wagging) |
| 1383 | $\delta_{sym}CH_3$ |
| 1467 | $\delta_{asym}CH_3$   $\delta CH_2$ (scissoring) |
| 2800 | $\nu_{sym}CH_2$ |
| 2876 | $\nu_{sym}CH_3$ |
| 2936 | $\nu_{asym}CH_2$ |
| 2972 | $\nu_{asym}CH_3$ |

[a] $\gamma$, out-of-plane bending vibration; $\delta$, in-plane bending vibration; $\nu$, stretching vibration or elongation bond vibration.

During the first hour of the reaction the widening of the two absorption bands at 1420–1350 and 1600–1550 cm$^{-1}$ indicates the formation of carboxylate groups.

The decrease of the band at 912 cm$^{-1}$, notably during the first hour of the reaction, would indicate automatically a consumption of epoxy groups. However, despite the considerable decrease of this band, the two bands at 1600–1550 and 1420–1350 cm$^{-1}$ remained intense. Otherwise, the band at 1126 cm$^{-1}$, characteristic of ethers, appeared only after postcuring (96 h at 100°C) and with a very low intensity. Therefore the etherification reaction does not occur during the 150 min of the cure reaction.

After the decrease of the band at 912 cm$^{-1}$ during the cure reaction (150 min), we noticed that this band remained unchanged after the postcure. The residual band can be attributed to the presence of alkene (SAA1). We also observed a decreasing band intensity at 1420–1350 and 1600–1550 cm$^{-1}$ after increasing during the reaction (150 min), and increasing band intensity both at 1184–1156 and at 3600–3100 cm$^{-1}$, characteristic of hydroxyls. All these changes indicate that, during postcure, a polyaddition esterification reaction also occurred. The band at 912 cm$^{-1}$ remained unchanged, whereas the cure reaction continued, indicating that the epoxy rings were always present but in the form of acid/epoxide/amine intermediary complexes. The formation of these complexes is corroborated by the considerable decrease in the band intensity of amine (1068 cm$^{-1}$) during the first hour of the reaction. The mechanism would include an initiation step with formation of intermediary complexes[16,17] and a step of crosslinked network formation. Therefore, the main reaction during 150 min is a polyaddition esterification reaction after formation of intermediary complexes.

### System SAA3/DGEBA

During the cure of SAA3/DGEBA, we observed a progressive decreasing of band intensity at 914 cm$^{-1}$, characteristic of epoxy rings. The decrease was fast during the first hour of the reaction, then became

## TABLE V
### Attribution of Frequency Bands of DGEBA

| Wavenumber (cm$^{-1}$) | Attribution[a] |
|---|---|
| 760–770 | $\gamma CH_{2\ r}$ (rocking) + $\gamma C—H$ of the disubstituted benzene; 1-4 substituted benzene (four adjacent hydrogens) |
| 831 | $\gamma C—H$ of the 1-4 substituted benzene + $\gamma CH_{2\ r}$ of the epoxide group |
| 915 | Characteristic vibration of the epoxide ring corresponding to $\nu_{asym}$ $\overset{C—C}{\diagdown\diagup}$ $O$ |
| 1036 | $\delta C—H$ of the 1-4 substituted benzene + $\nu_{sym}C—O—C$ in the case of an aromatic ether |
| 1085 | $\delta C—H$ benzenic |
| 1132 | $\nu C—O$ of the epoxide ring |
| 1155, 1184 | $\delta C—H$ benzenic |
| 1247 | $\nu_{sym}$ $\overset{C—C}{\diagdown\diagup}$ $O$ of the epoxide ring + $\nu_{asym}$ $C—O—C$ in the case of an aromatic ether |
| 1297 | $\gamma CH_{2\ t} + \gamma CH_{2\ w}$ (twisting and wagging) |
| 1347 | $\delta CH_{2\ t}$ (twisting of the epoxy group) |
| 1363, 1386 | $\delta_{sym}CH_3$, doublet in the case of *gem*-dimethyl groups |
| 1458 | $\delta CH_2$ (scissoring) + $\delta_{asym}CH_3 + \nu C=C$ of the 1-4 substituted benzene |
| 1508, 1582, 1608 | $\nu C=C$ of the 1-4 substituted benzene |
| 1650–2000 | Overtone and combination tone bands. Characteristic bands of substitution pattern |
| 2873, 2930, 2969 | $\nu C—H$ aliphatic |
| 3000 | $\nu C—H$ of the epoxy group |
| 3038, 3058 | $\nu C—H$ aromatic |

[a] See Table IV.

**TABLE VI**
**Attribution of Frequency Bands of SAA1 Copolymer**

| Wavenumber (cm$^{-1}$) | Attribution[a] |
|---|---|
| 543 | $\delta$H—C—C and $\delta$C—C—C skeletal |
| 700 | $\gamma$C—H of the monosubstituted benzene (five adjacent hydrogenss) |
| 760 | $\gamma$C—H of the monosubstituted benzene + $\gamma$CH$_{2\,r}$ (rocking) |
| 842–982 | $\gamma$C—H in the case of alkene (double bonds formed during termination: synthesis of the copolymer) + $\nu$C—C + $\gamma$O—H acid |
| 1030, 1068 | $\delta$C—H of the substituted benzene |
| 1157, 1183 | $\delta$C—H of the substituted benzene |
| 1200–1243 | Characteristic doublet in the case of the aliphatic long-chain acids corresponds to $\nu$C—O |
| 1290 | $\gamma$CH$_{2\,t}$ + $\gamma$CH$_{2\,w}$ + $\delta$C—H in the case of alkene |
| 1366 | $\delta$C—H in the case of substituted alkene |
| 1420 | $\delta$C—OH acid |
| 1453 | $\nu$C=C of the monosubstituted benzene + $\delta$CH$_2$ (scissoring) |
| 1493, 1584, 1603 | $\nu$C=C of the monosubstituted benzene |
| 1704 | $\nu$C=O in the case of dimerized carboxyls (associates) |
| 1733 | $\nu$C=O in the case of monomeric carboxyls (free) |
| 1650–2000 | Overtone and combination tone bands. Characteristic bands of substitution pattern. |
| 2400–3600 | $\nu$O—H acid |
| 2857, 2926 | $\nu_{sym}$CH$_2$ + $\nu_{asym}$CH$_2$ |
| 3003 | $\nu$C—H in the case of alkene |
| 3027, 3061, 3084 | $\nu$C—H aromatic |

[a] See Table IV.

slow. We also observed decreasing intensity of the characteristic band of amine ($\nu$C—N) at 1066 cm$^{-1}$, and decreasing intensity of the two characteristic bands of carboxylates at 1600–1550 and 1420–1350 cm$^{-1}$ as well as a decrease of the characteristic band of the acid O—H at 3700–3100 cm$^{-1}$. Simultaneously, the intensity of the two characteristic bands of the esters at 1184–1155 and 1712 cm$^{-1}$ increased. These changes indicate that addition esterification reaction occurred. Furthermore, we observed only a slight decrease but not total disappearance of the OH band at 3700–3100 cm$^{-1}$ during the reaction. The presence of the OH band during the reaction is attributed to the fact that after consumption of the acid OH, the alcohol OH is formed.

During postcuring, the intensity of the epoxy band at 914 cm$^{-1}$ decreased but did not disappear. Furthermore, we noticed the appearance of the ether band at 1126 cm$^{-1}$ with very low intensity and an increase of the band intensity of the hydroxyls at 3700–3100 cm$^{-1}$.

According to the obtained results, the SAA3/DGEBA system gives a series of addition esterification reactions during cure, and a slight etherification reaction occurs during the postcure.

## System SAA5/DGEBA

During cure (150 min) of the SAA5/DGEBA system, a decrease of the epoxy band at 915 cm$^{-1}$ was observed. After the first hour of reaction, the acid O—H band (3700–3100 cm$^{-1}$) disappeared. We also noticed a de-

creasing intensity of the two characteristic bands of carboxylates at 1600–1550 and 1420–1350 cm$^{-1}$ and an increase of the two bands of esters (1184–1155 and 1712 cm$^{-1}$). These changes suggest an addition esterification reaction. However, the characteristic hydroxyl band produced by the reaction, located in the same zone as that of the free acid O—H (3700–3100 cm$^{-1}$), did not appear even after total disappearance of the free acid O—H band. We noticed the appearance of the characteristic ether band at 1125 cm$^{-1}$. An etherification reaction that consumes the hydroxyls produced by the addition esterification reaction occurs in parallel.

During postcuring, 96 h at 100°C, we observed a decrease of the epoxy band at 915 cm$^{-1}$, appearance of a hydroxyl band at 3700–3100 cm$^{-1}$, and an increase of intensity band of esters at 1800–1700 and 1250–1184–1157 cm$^{-1}$. The characteristic band of ether changed only slightly during this phase. During postcuring, the reaction was almost exclusively an addition esterification reaction.

The SAA5/DGEBA system undergoes an addition esterification reaction, followed by an etherification reaction of hydroxyls generated by the addition esterification.

## System SAA6/DGEBA

In this system, the main reaction was the addition esterification reaction, with a parallel secondary reaction, the condensation esterification reaction. Besides a decrease of the epoxy band and an increase of the two
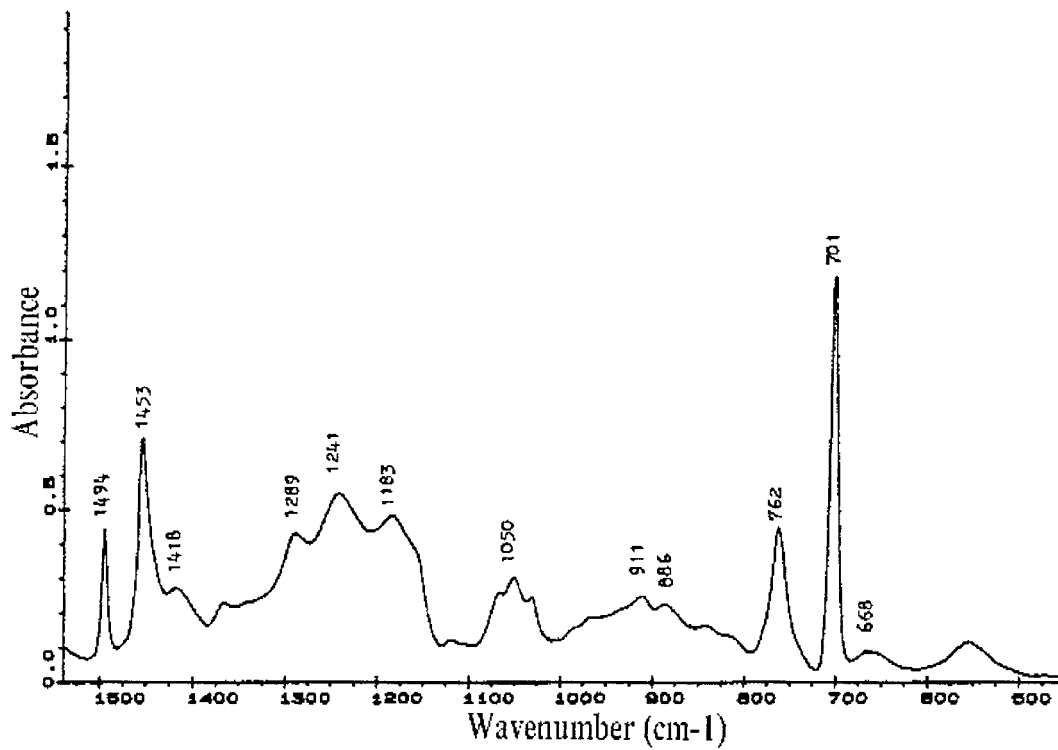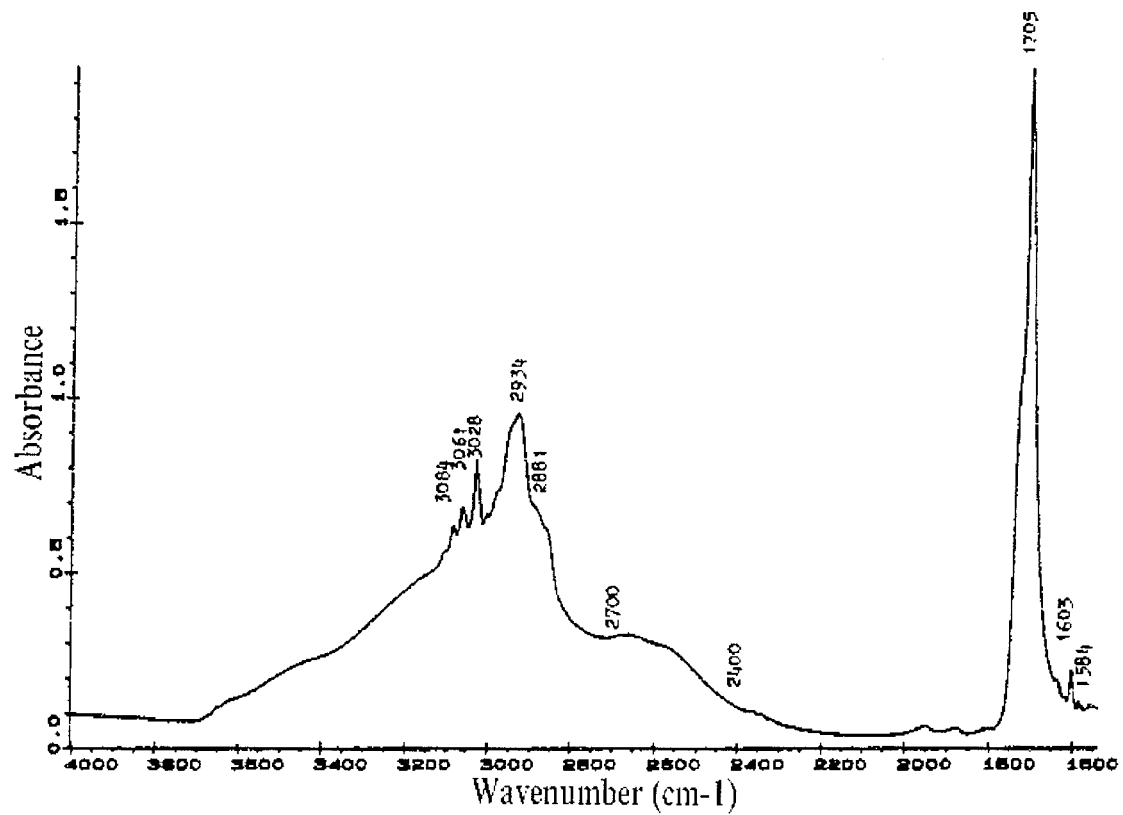
**Figure 4**  FTIR spectrum of the SAA3 copolymer.

**TABLE VII**
**Attribution of Frequency Bands of SAA3 Copolymer**

| Wavenumber (cm$^{-1}$) | Attribution[a] |
|---|---|
| 700 | $\gamma$C—H of the monosubstituted benzene (five adjacent hydrogens) |
| 760 | $\gamma$C—H of the monosubstituted benzene + $\gamma$CH$_{2\ r}$ (rocking) |
| 842, 911–1000 | $\gamma$C—H in the case of alkene (formed at termination during synthesis of copolymer) + $\nu$C—C + $\gamma$O—H acid |
| 1183, 1241 | Characteristic doublet in the case of the aliphatic long-chain acids corresponds to $\nu$C—O |
| 1241–1289 | $\nu$C—O acid + $\gamma$CH$_{2\ t}$ + $\gamma$CH$_{2\ w}$ |
| 1418 | $\delta$C—OH acid |
| 1453 | $\nu$C=C of the monosubstituted benzene + $\delta$CH$_2$ (scissoring) |
| 1494, 1584, 1603 | $\nu$C=C of the monosubstituted benzene |
| 1705 | $\nu$C=O in the case of dimerized carboxyls (associates) |
| 1650–2000 | Overtone and combination tone bands. Characteristic bands of substitution pattern. |
| 2400–3700 | $\nu$O—H acid |
| 2881, 2934 | $\nu$C—H aliphatic |
| 3028, 3061, 3084 | $\nu$C—H aromatic |

[a] See Table IV.

ester bands, the carboxyl bands (3700–3000 cm$^{-1}$) disappeared after 10 min of the reaction. The hydroxyl band, situated in the same zone, appeared only during the postcure. The hydroxyls formed during the reaction would react with the carboxylates to give a condensation esterification reaction. Indeed, the ether

**TABLE VIII**
**Attribution of Frequency Bands of the SAA1/DGEBA System**

| Wavenumber (cm$^{-1}$) | Attribution[a] |
|---|---|
| 702 | $\gamma$C—H of the monosubstituted benzene |
| 763 | $\gamma$C—H of the monosubstituted benzene + $\gamma$CH$_{2\ r}$ (rocking) (SAA1, DGEBA, TEA) |
| 831 | $\gamma$C—H of the disubstituted benzene; 1-4 substituted benzene (DGEBA) + $\gamma$CH$_{2\ r}$ of the epoxide ring (DGEBA) |
| 912 | $\nu_{asym}$ $\overset{C—C}{\underset{O}{\diagdown\diagup}}$ of the epoxide ring (DGEBA) + $\delta$C—H in the case of alkene (SAA1) |
| 1036 | $\delta$C—H of the substituted benzene + $\nu_{sym}$C—O—C in the case of an aromatic ether (DGEBA) |
| 1068 | $\delta$C—H of the substituted benzene + $\nu$C—N (TEA) |
| 1156, 1184 | $\delta$C—H of the substituted benzene (SAA1, DGEBA) |
| 1230–1248 | $\nu$C—O (SAA1) + $\nu_{sym}$ $\overset{C—C}{\underset{O}{\diagdown\diagup}}$ (DGEBA) + $\nu_{asym}$C—O—C in the case of an aromatic ether (DGEBA) |
| 1295 | $\gamma$CH$_{2\ t}$ + $\gamma$CH$_{2\ w}$ (SAA1, DGEBA, TEA) |
| 1348 | $\delta$CH$_{2\ t}$ (twisting of the epoxy group) |
| 1362, 1385 | Doublet corresponding to $\delta_{sym}$CH$_3$ (DGEBA, TEA) |
| 1385–1420 | $\delta$C—OH acid (SAA1) |
| 1453 | $\nu$C=C of the substituted benzene (SAA1, DGEBA) + $\delta_{asym}$CH$_3$ (DGEBA, TEA) + $\delta$CH$_2$ (scissoring) (SAA1, DGEBA) |
| 1493 | $\nu$C=C of the monosubstituted benzene (SAA1) |
| 1510 | $\nu$C=C of the 1-4 substituted benzene (DGEBA) |
| 1582, 1602 | Doublet corresponding to $\nu$C=C of the substituted benzene (SAA1, DGEBA) |
| 1727 | $\nu$C=O acid (free and associates) |
| 1650–2000 | Overtone and combination tone bands |
| 2200–3600 | $\nu$O—H acid |
| 2856 | $\nu_{sym}$CH$_2$ |
| 2926 | $\nu_{asym}$CH$_2$ + $\nu_{sym}$CH$_3$ |
| 2969 | $\nu_{asym}$CH$_3$ |
| 3001 | $\nu$C—H of the epoxide group |
| 3027, 3061, 3084 | $\nu$C—H aromatic |

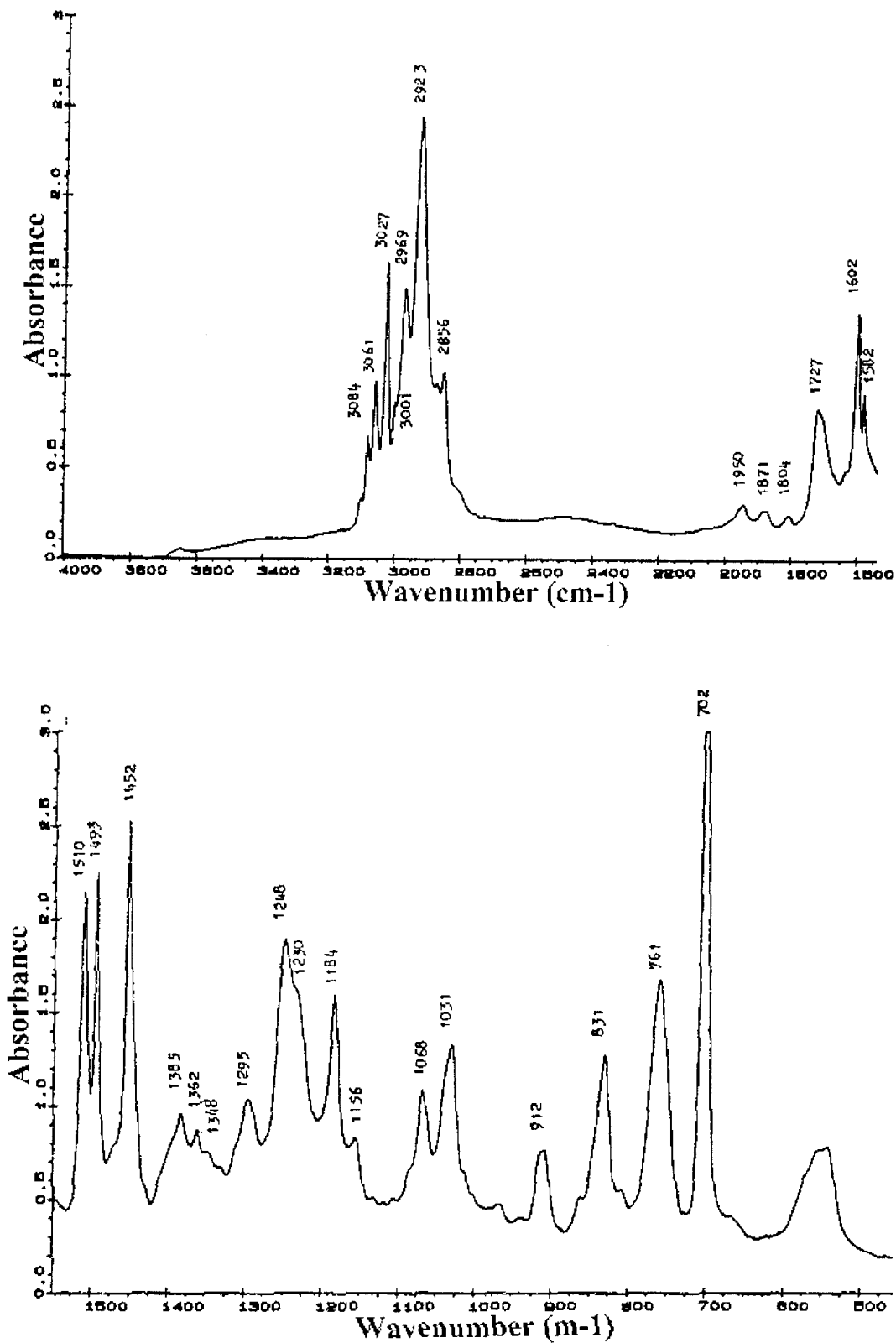[a] See Table IV.

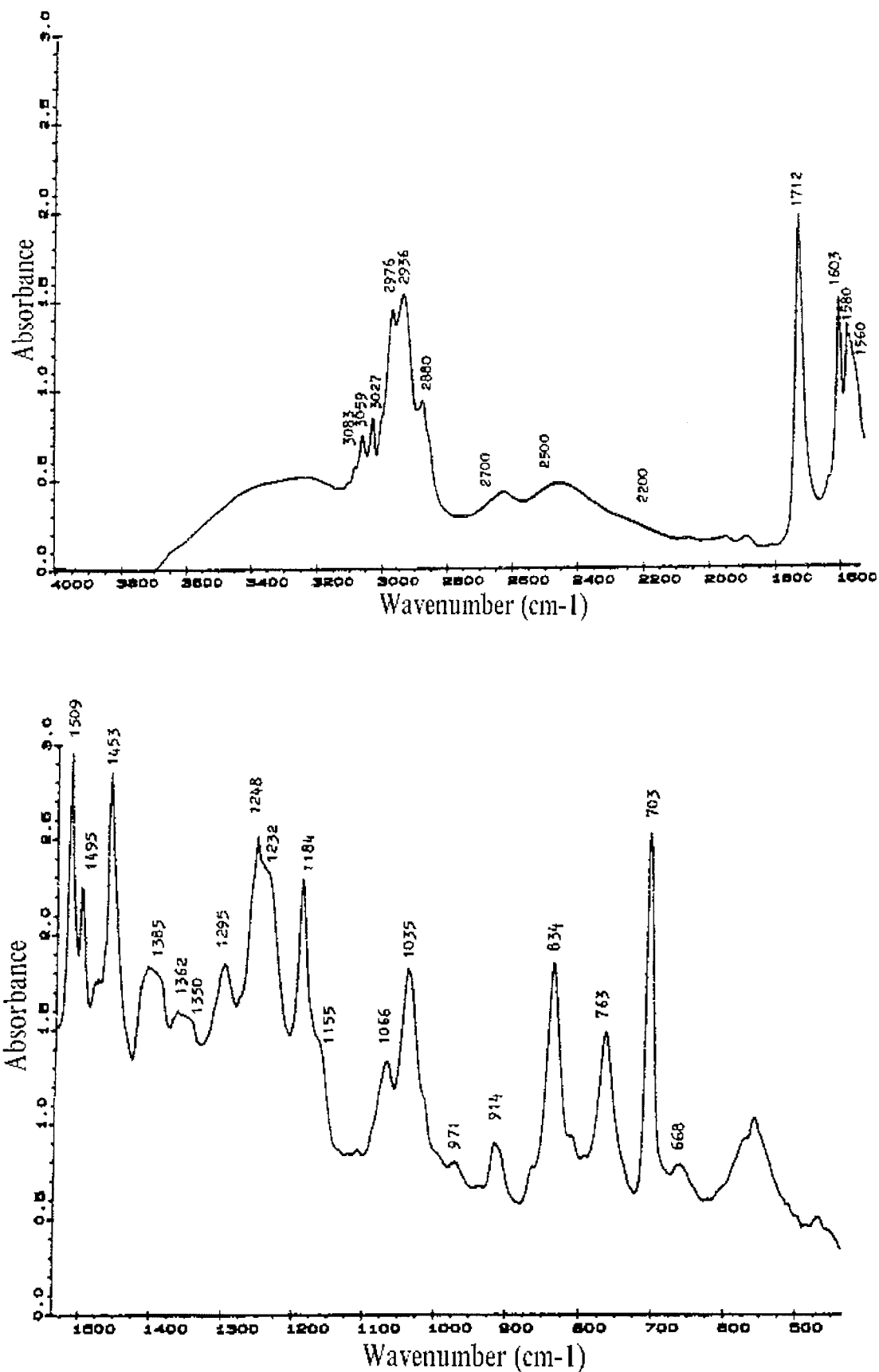**Figure 5**     FTIR spectrum of the SAA1/DGEBA system.

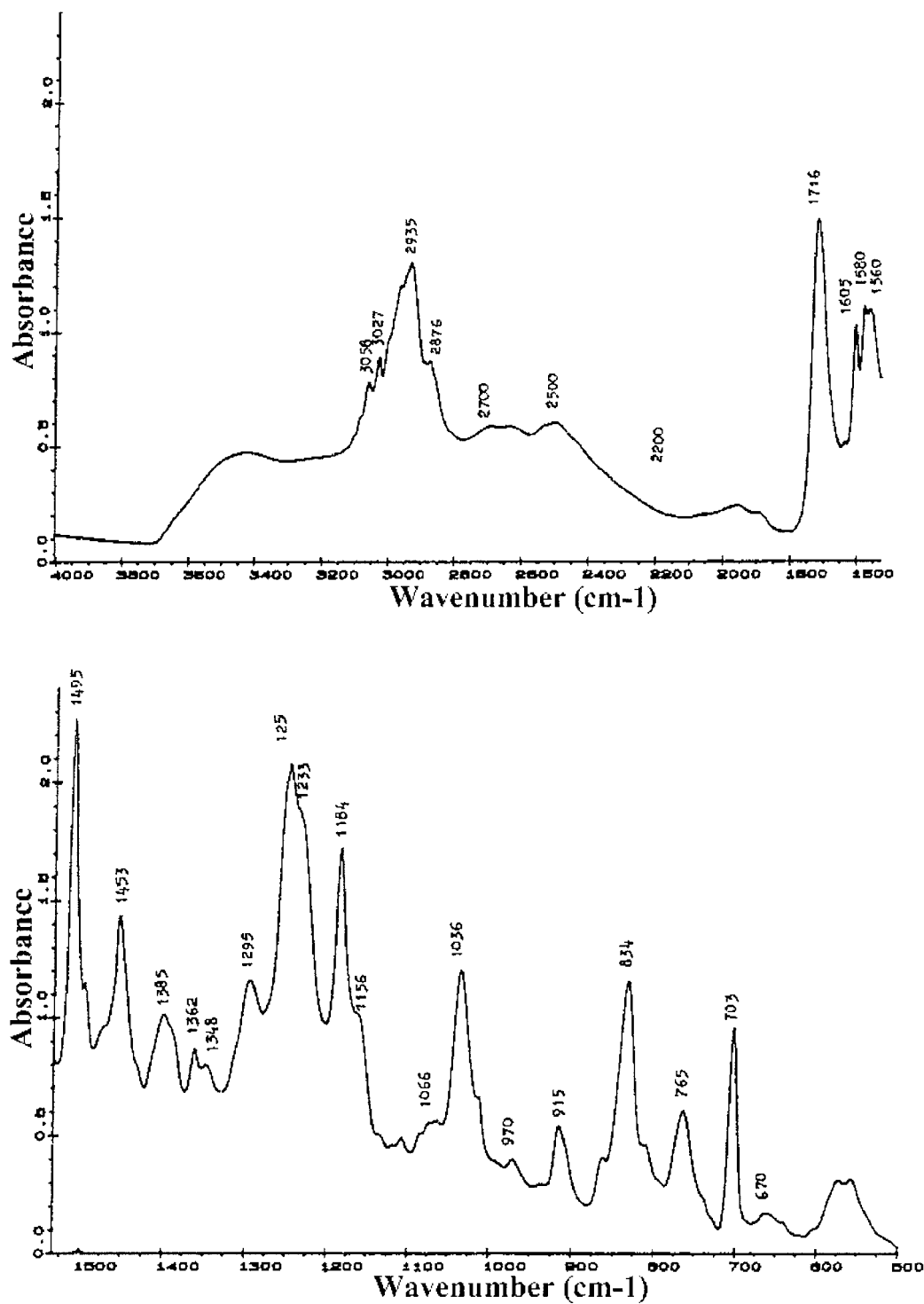**Figure 6** FTIR spectrum of the SAA3/DGEBA system.
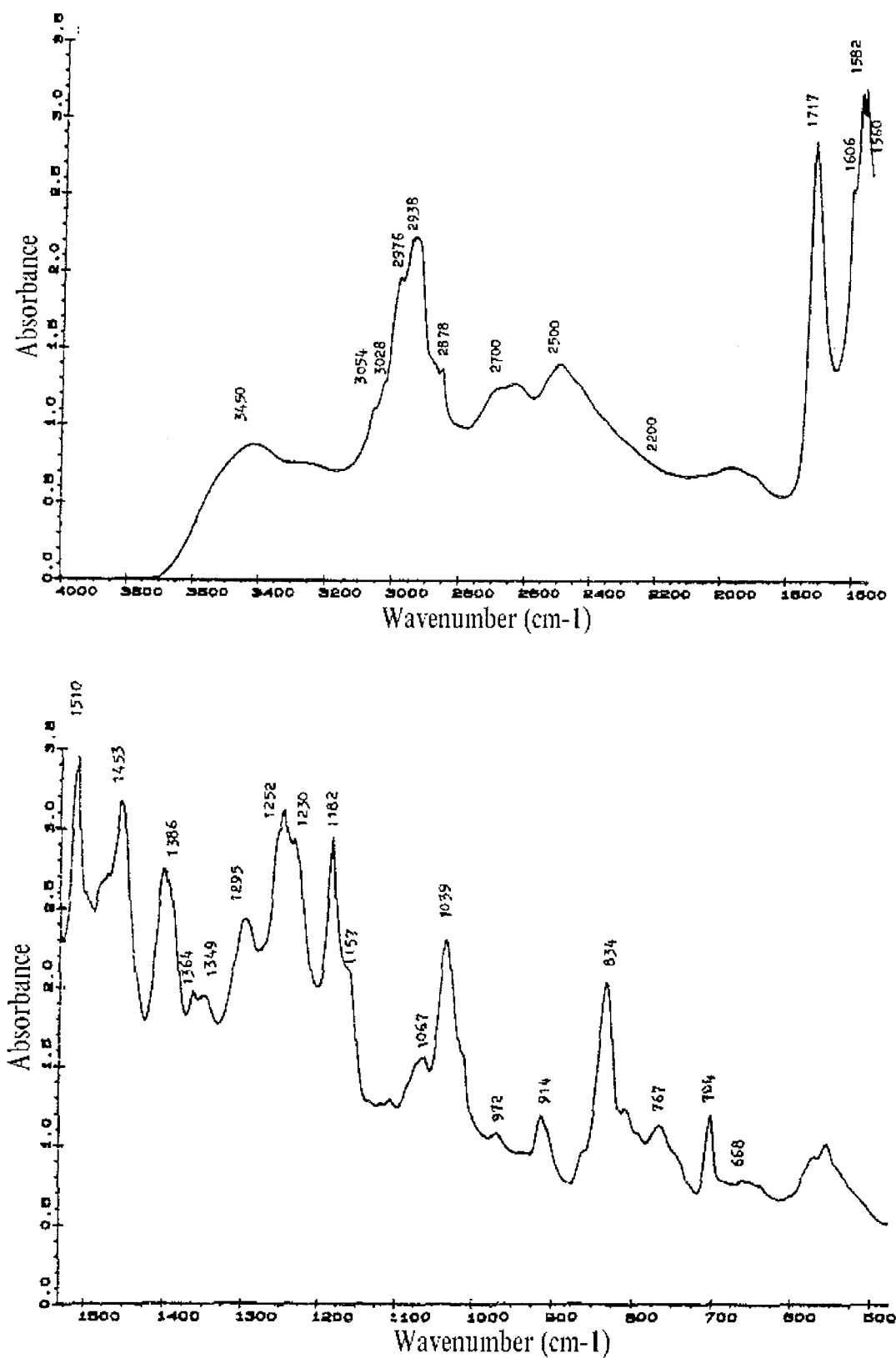
**Figure 7** FTIR spectrum of the SAA5/DGEBA system.

**Figure 8** FTIR spectrum of the SAA6/DGEBA system.

**TABLE IX**
**Attribution of Frequency Bands of the SAA3/DGEBA System**

| Wavenumber (cm$^{-1}$) | Attribution[a] |
|---|---|
| 668 | $\delta COO^-$ in the case of dimers |
| 702 | $\gamma C$—H of the monosubstituted benzene |
| 763 | $\gamma C$—H of the monosubstituted benzene + $\gamma CH_{2\,r}$ (rocking) |
| 834 | $\gamma C$—H of the dissubstituted benzene; 1-4 substituted benzene (DGEBA) + $\gamma CH_{2\,r}$ of the epoxide ring (DGEBA) |
| 914 | $\nu_{asym}$ $\overset{C-C}{\underset{O}{\diagdown\diagup}}$ (DGEBA) + $\delta C$—H in the case of alkene (SAA1) |
| 1035 | $\delta C$—H of the substituted benzene + $\nu_{sym}C$—O—C in the aromatic ether case (DGEBA) |
| 1066 | $\delta C$—H of the substituted benzene + $\nu C$—N (TEA) |
| 1184 | $\delta C$—H of the substituted benzene (SAA3, DGEBA) + $\nu C$—O (SAA3) |
| 1232–1248 | $\nu C$—O (SAA3) + $\nu_{sym}$ $\overset{C-C}{\underset{O}{\diagdown\diagup}}$ (DGEBA) + $\nu_{asym}C$—O—C in the aromatic ether case (DGEBA) |
| 1295 | $\gamma CH_{2\,t}$ + $\gamma CH_{2\,w}$ (SAA3, DGEBA, TEA) |
| 1350–1362 | $\delta CH_{2\,t}$ (twisting of the epoxy group) + $\delta_{sym}CH_3$ (DGEBA, TEA) + $\nu_{sym}COO^-$ (in the case of carboxylates ions) (SAA3) |
| 1385 | + $\delta_{sym}CH_3$ (splitting of 1362 cm$^{-1}$) |
| 1385–1420 | $\nu_{sym}COO^-$ (in the case of carboxylates ions) (SAA3) + $\delta C$—OH acid (SAA3) |
| 1454 | $\nu C$=C of the substituted benzene (SAA1, DGEBA) + $\delta_{asym}CH_3$ (DGEBA, TEA) + $\delta CH_2$ (scissoring) (SAA3, DGEBA) |
| 1494, 1509, 1581, 1603 | $\nu C$=C benzenic |
| 1650–1580 | $\nu_{asym}COO^-$ (SAA3) + $\delta NH^+$ |
| 1650–2000 | Harmonic and combinations of the benzene |
| 1712 | $\nu C$=O acid (dimerized) |
| 2200–2800 | $\nu NH^+$ (TEA) |
| 2200–2700 | $\nu O$—H acid |
| 2880, 2936, 2976 | $\nu C$—H aliphatic |
| 3027, 3059, 3083 | $\nu C$—H aromatic |

[a] See Table IV.

band at 1126 cm$^{-1}$, which appeared only during post-cure, indicated that there was no etherification reaction during the kinetics (150 min).

The addition esterification reaction was still predominant during the postcuring (appearance of hydroxyl band and increase of characteristic ester bands), followed this time by an etherification reaction, as shown by the appearance of the ether band (1126 cm$^{-1}$) and disappearance of the epoxy band (914 cm$^{-1}$). This change in the course of the reaction is attributed to significant consumption of the carboxylates during the kinetics (addition and condensation esterification) entailing the remainder of the epoxide rings available to an etherification reaction.

Figures 13–15 give the epoxy fractional conversion versus time of the three systems, SAA3/DGEBA, SAA5/DGEBA, and SAA6/DGEBA, at different temperatures. Table X represents the degree of conversion reached after 120 min of reaction for these three systems.

The change of shape curve of the SAA6/DGEBA system, as represented in Figure 15, is probably attributable to the secondary reaction (condensation esterification) producing water molecules. The O—H vibration bands of H$_2$O (3652, 3756, and 1595 cm$^{-1}$) are not detected in the IR spectrum because of the gaseous state of the water molecules at the working temperatures.

## CONCLUSIONS

For all systems studied, after 120 min of reaction, the reactivity became very low, even with significant residual epoxy groups. The growth of a tridimensional network leads to steric hindrance, which reduces the rate and prevents the reaction from continuing.

For the two systems SAA1/DGEBA and SAA3/DGEBA, the reaction is selectively addition esterification. In the two systems SAA5/DGEBA and SAA6/

**TABLE X**
**Degree of Conversion after 120 min of Reaction**

| System | $T$ (°C) | Degree of conversion |
|---|---|---|
| SAA3/DGEBA | 90 | 0.60 |
|  | 85 | 0.52 |
| SAA5/DGEBA | 95 | 0.64 |
|  | 85 | 0.28 |
| SAA6/DGEBA | 95 | 0.44 |
|  | 85 | 0.25 |
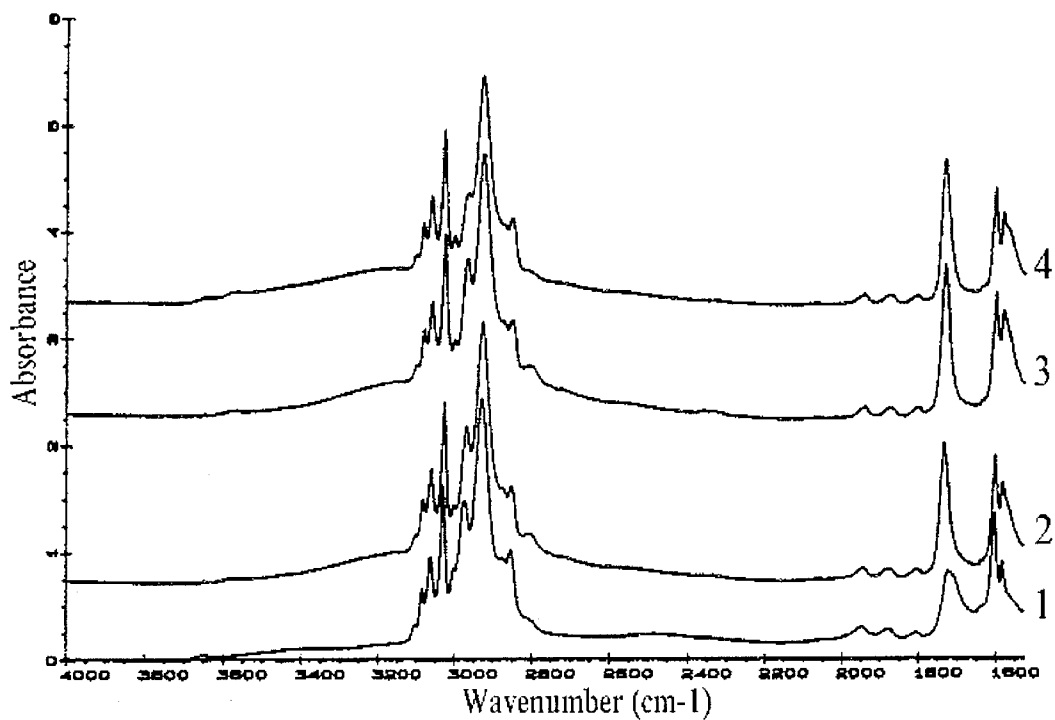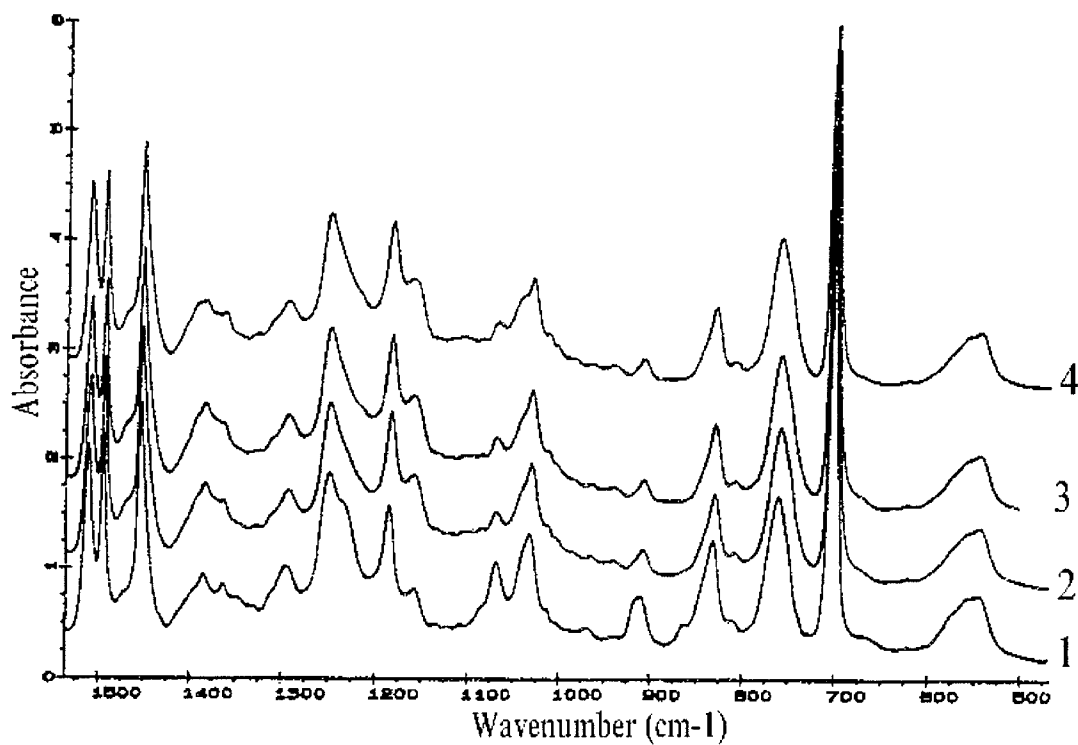
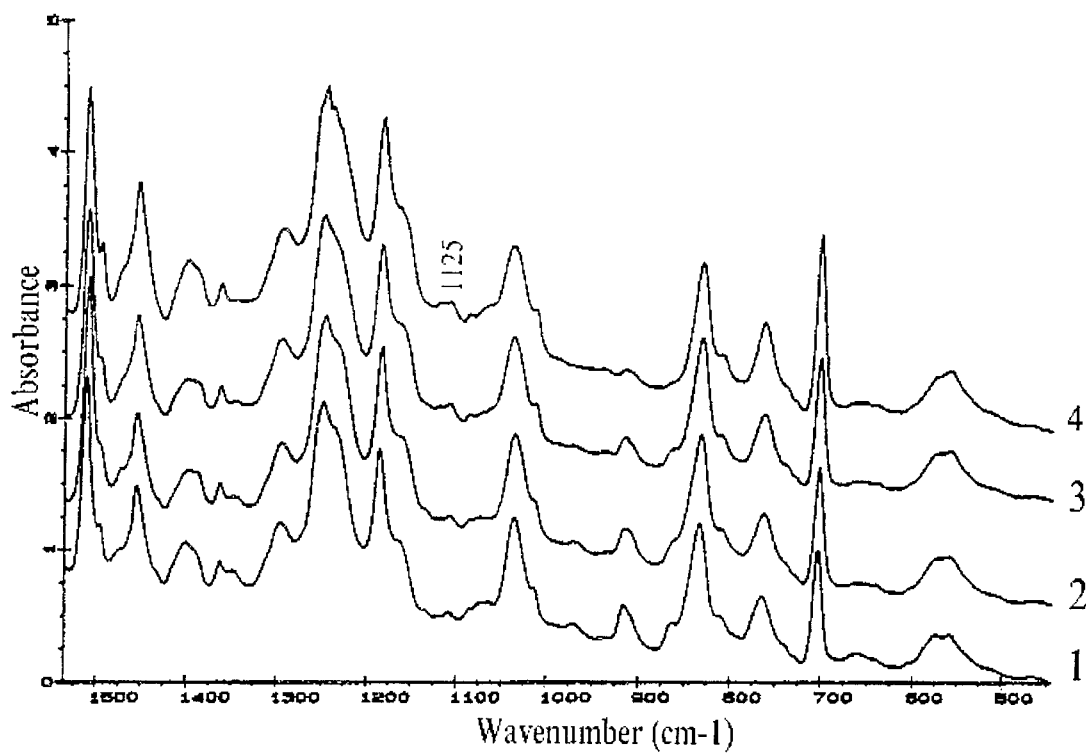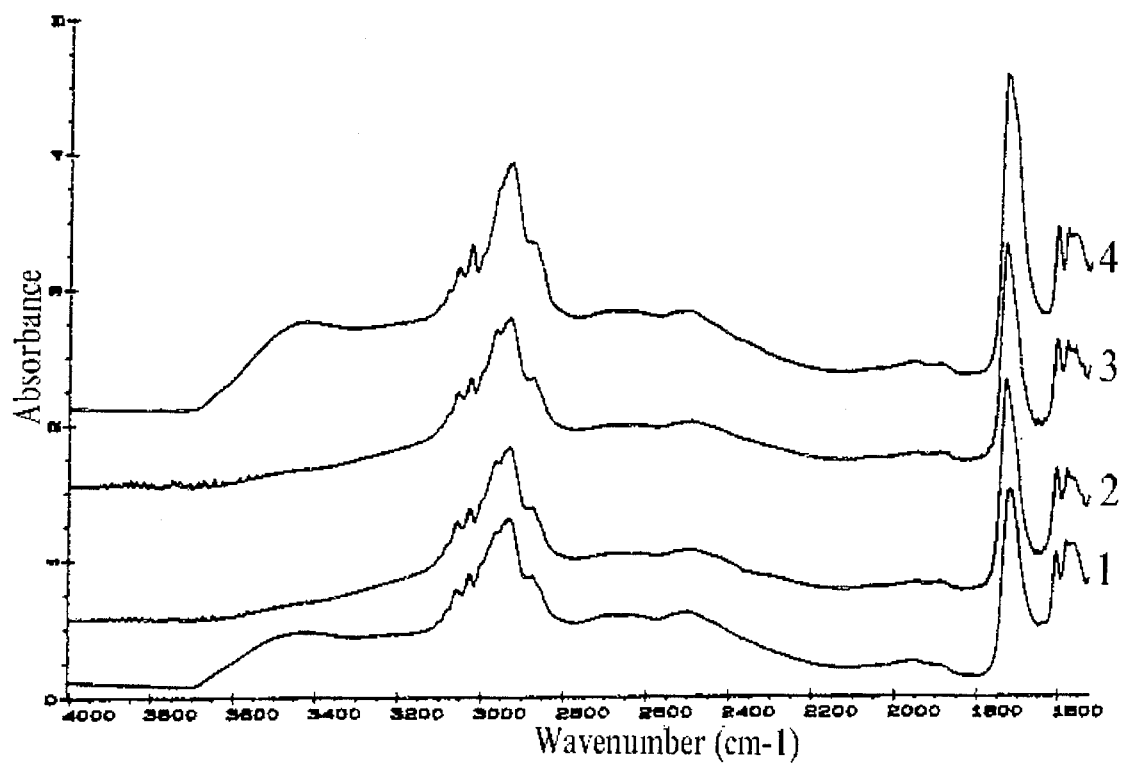**Figure 9** FTIR spectrum of the SAA1/DGEBA system: (1) $t = 0$; (2) $t = 60$ min at $T = 110°C$; (3) $t = 150$ min at $T = 110°C$; (4) postcuring, 96 h at 100°C.
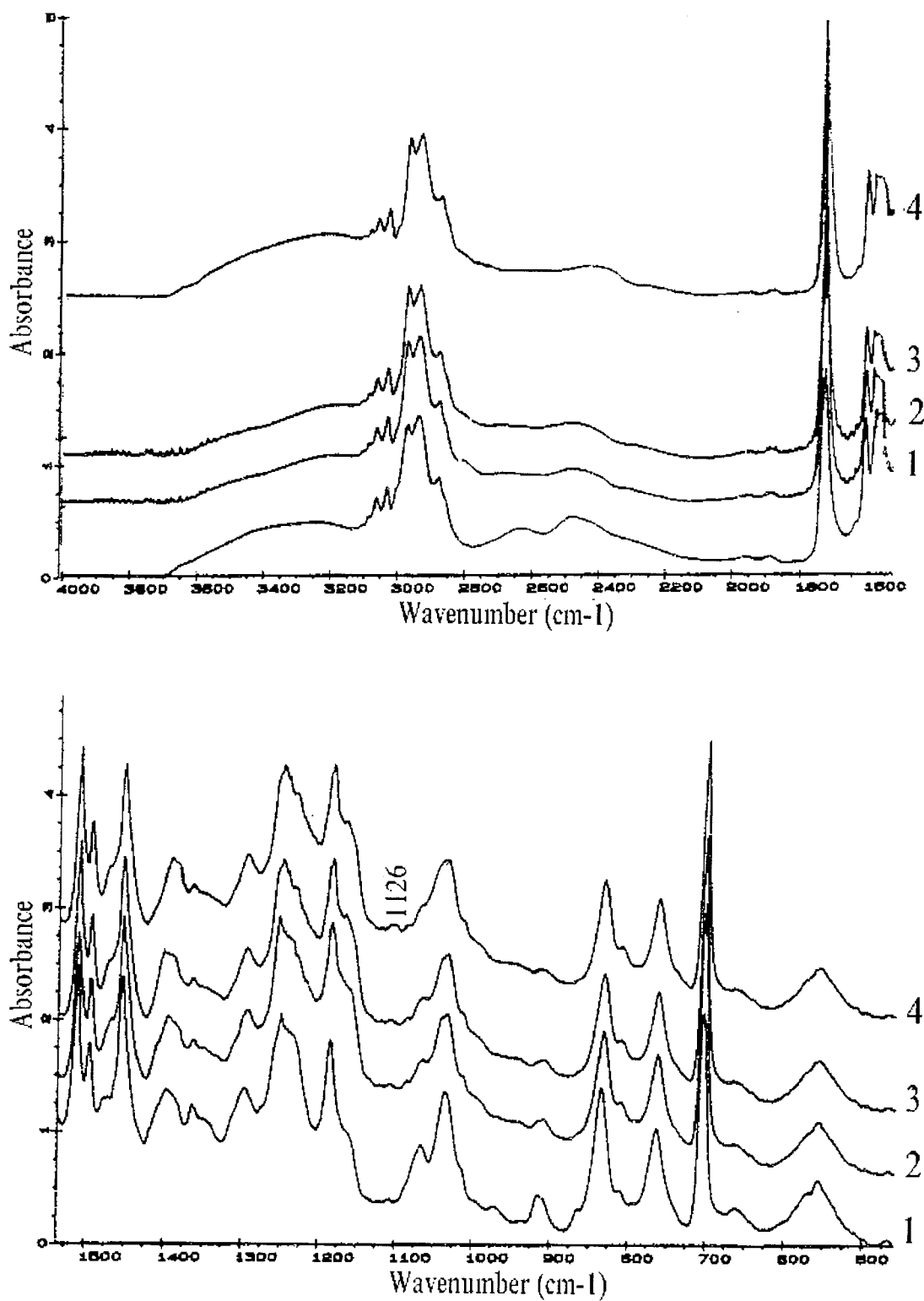
**Figure 10**    FTIR spectrum of the SAA3/DGEBA system: (1) $t = 0$; (2) $t = 60$ min at $T = 90°C$; (3) $t = 150$ min at $T = 90°C$; (4) postcuring, 96 h at 100°C.
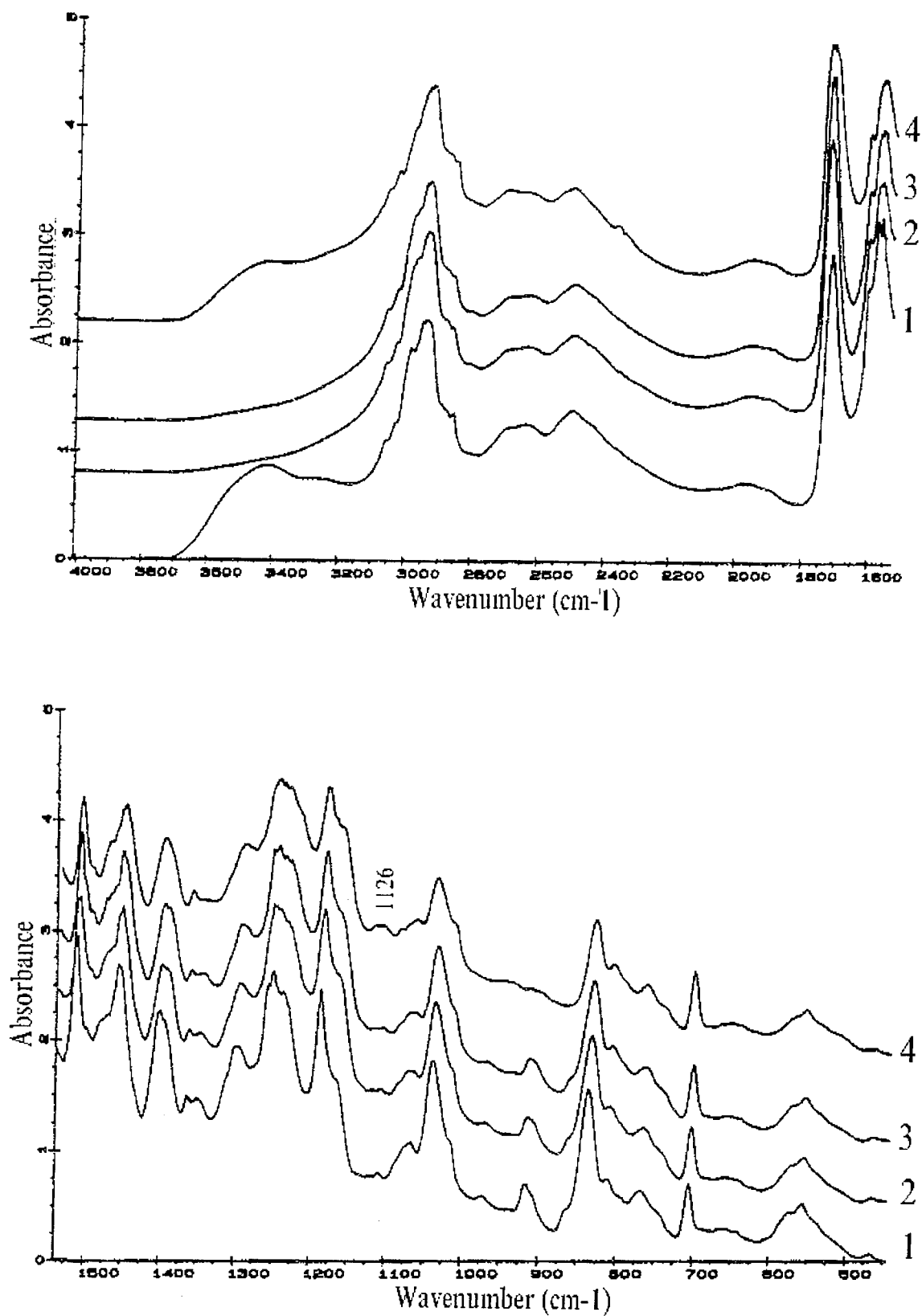
**Figure 11** FTIR spectrum of the SAA5/DGEBA system: (1) $t = 0$; (2) $t = 60$ min at $T = 100°C$; (3) $t = 150$ min at $T = 100°C$; (4) postcuring, 96 h at 100°C.

**Figure 12**    FTIR spectrum of the SAA6/DGEBA system: (1) $t = 0$; (2) $t = 60$ min at $T = 95°C$; (3) $t = 150$ min at $T = 95°C$; (4) postcuring, 96 h at 100°C.

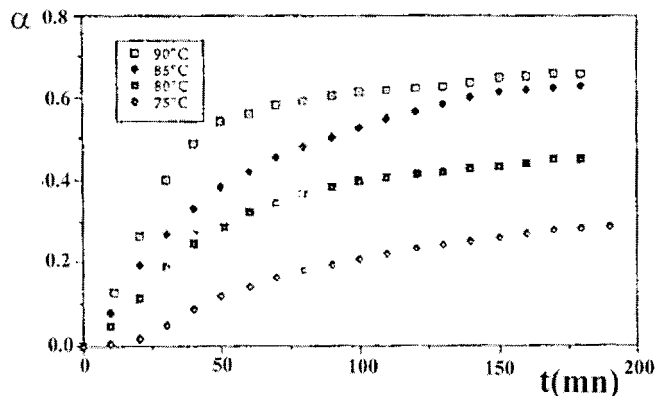**Figure 13** $\alpha = f(t)$ at different temperatures of the SAA3/DGEBA system.



**Figure 15** $\alpha = f(t)$ at different temperatures of the SAA6/DGEBA system.

DGEBA, etherification and condensation esterification are in competition with addition esterification. This difference of reactivity between SAA1/DGEBA, SAA3/DGEBA, SAA5/DGEBA, and SAA6/DGEBA is linked both to the acid group composition in the copolymer and to the chain structure.

Lower acid composition in the copolymers (SAA1 and SAA3) favors the polyaddition esterification reaction generating monoester and hydroxyl groups. The higher acid compositions (SAA5 and SAA6) entail many carboxyl groups in the polymeric chain. The difference in the mechanism between the two corresponding systems, addition esterification and etherification reaction for SAA5/DGEBA and addition esterification and condensation esterification for SAA6/DGEBA, is ascribed to the fact that, for the lat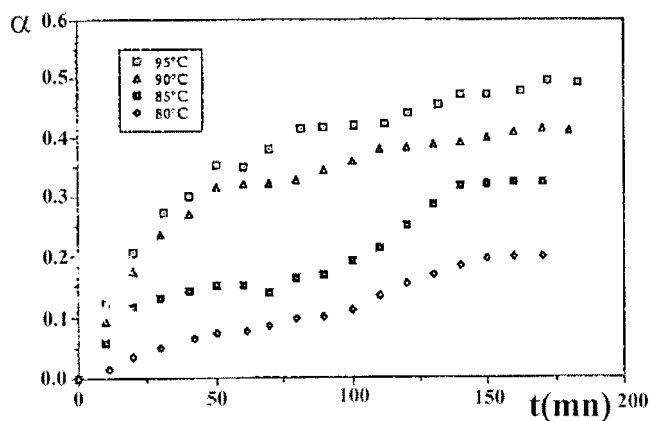ter, the carboxyl and generated hydroxyl groups are close to each other and the condensation esterification is favored. For SAA5, the generated hydroxyls are more spaced from the residual carboxyls, so that in this case the etherification reaction is favored.

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**Figure 14** $\alpha = f(t)$ at different temperatures of the SAA5/DGEBA system.