Isothermal Curing of a Dicyanate Ester Monomer Up to the Gel Point as Studied by Size Exclusion Chromatography

Ileana B. Recalde[a]; Agustín Campos[a]; Clara M. Gómez[a]; Iñaki Mondragon[b]; Isabel Harismendy[b]

[a] Departament de Química Física, Institut de Ciència dels Materials, València, Spain [b] Dpto. Ing. Química y M. Ambiente, Escuela Univ, San Sebastián, Spain

PLEASE SCROLL DOWN FOR ARTICLE

Isothermal Curing of a Dicyanate Ester Monomer Up to the Gel Point as Studied by Size Exclusion Chromatography

**Ileana B. Recalde, Agustín Campos,
and Clara M. Gómez**
Departament de Química Física and Institut de Ciència
dels Materials, València, Spain

Iñaki Mondragon and Isabel Harismendy
Dpto. Ing. Química y M. Ambiente, Escuela Univ.
Ingenieria T. Industrial, San Sebastián, Spain

*The curing of a dicyanate ester of bisphenol A with and without
cobalt(II) acetylacetonate/nonylphenol and with copper(II) acetylace-
tonate/nonylphenol catalysts was analyzed until the gel point using size
exclusion chromatography (SEC). This technique can be used to
determine the overall dicyanate conversion as a function of time in the
pre-gel state at different curing temperatures (between 130°C and 220°C
according to the system). The results have been compared with those
obtained by curing the same system by differential scanning calorimetry,
showing good agreement. The data obtained indicate that the rate of
reaction in the pre-gel stage is kinetically controlled and can be fitted
with a second-order reaction with respect to the disappearance of
cyanate groups. Apparent activation energies in the range 69–72 kJ/mol
have been obtained from the rate constants. Experimental data on
gelation times give activation energies around 70–77 kJ/mol, in accord
with previous values.*

481

INTRODUCTION

Cyanate resins are used as composites and in the electronic packaging industry because of their attractive mechanical and electric properties[1,2]. The cured material exhibits a high glass-transition temperature (T_g), low dielectric constant, good adhesion to metals at temperatures up to 250°C, and high fracture toughness, among other properties.

These resins cure by nonlinear step polymerization without condensation products upon increasing the temperature (> 200°C) (see Scheme 1.)[3–5]. However, the incorporation of a catalyst system (such as a transition metal complex and an alkyl phenol co-catalyst)[6,7] reduces the processing temperature by up to 90°C, without reduction of the matrix properties. The role of the transition metal is to gather cyanate groups via coordination while the hydroxyl group donates protons for imidocarbonate formation and step transfer.

In order to adopt a convenient cure schedule for a particular application, it is necessary to know the kinetics of network formation, the reaction extent at the gel point, the vitrification time at any temperature, the maximum achievable T_g, and the possible existence of degradation reactions. In particular, the processability of these resins depends critically on the rate and extent of polymerization under the processing conditions. Understanding the cure kinetics of these matrices becomes essential for defining process development. Different researchers have investigated the kinetics of these systems with and without catalyst systems, changing the cure temperature, in different atmospheres and using different techniques[1,8–10]. Results from different authors differ from one to another and seem to depend on the experimental conditions. The purpose of this work was to study the kinetics of cyclotrimerization of metal-catalyzed (cobalt and copper) and uncatalyzed bisphenol A-based cyanate ester resin (AroCy B10) until the gel point by size exclusion chromatography (SEC). The gel point delimits the processability of thermosetting resins; at this stage an insoluble portion appears.

This work is closely related with previous papers[11–13] carried out in our laboratory and introduces the cobalt catalyst that will be used in future work. The disappearance of the monomer peak has been used to follow the conversion of the dicyanate monomer in order to control the buildup of the network for industrial purposes. The kinetic data were analyzed and compared with those obtained by differential scanning calorimetry (DSC). The reproducibility of the technique has been tested. Gelation times and the corresponding conversion were determined. Activation energies were also calculated.

3
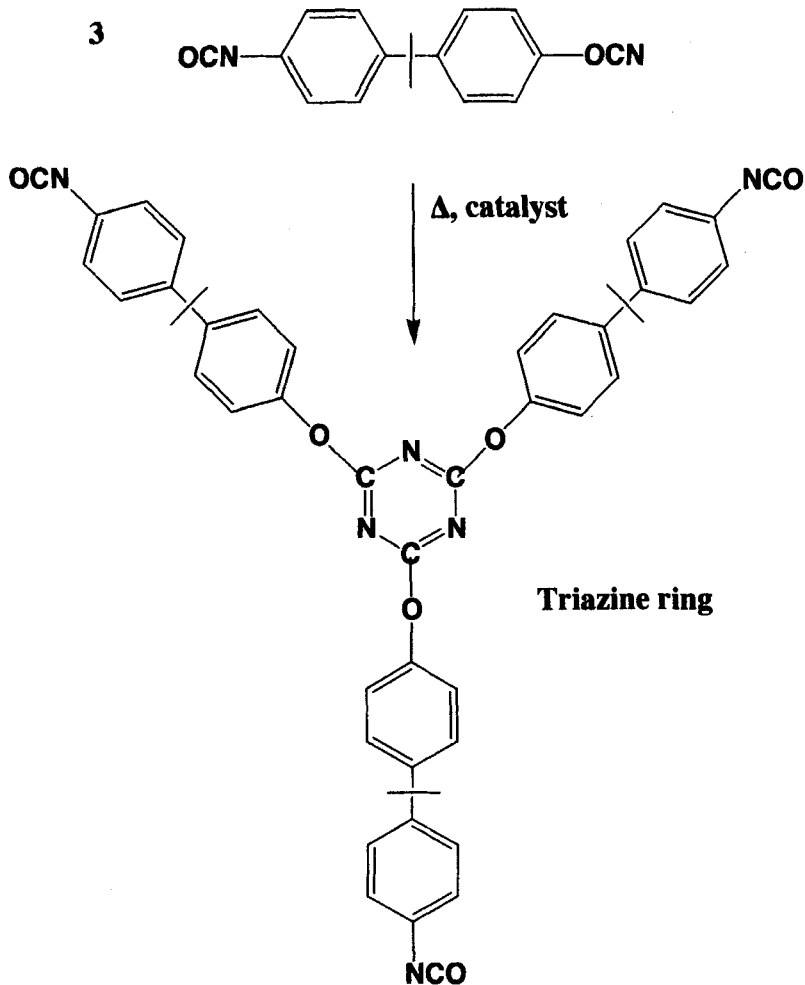
SCHEME 1 Polycyclotrimerization reaction of bisphenol A dicyanate to form triazine rings.

EXPERIMENTAL

Materials

In this study, two bisphenol A-based cyanate resin systems were used: the bisphenol-A dicyanate, (BADCy) (2,2′-bis(4-cyanatophenyl) iso-propylidene) monomer with the trade name AroCy B10, 99.5% purity,

and its prepolymer AroCy B30 (30% cyanate conversion), 95% purity, both supplied by Ciba-Geigy. The complex metals cobalt (II) acetylacetonate, $Co(AcAc)_2$, and copper (II) acetylacetonate, $Cu(AcAc)_2$ (99%) with the co-catalyst nonylphenol, NP (technical grade), all from Aldrich, formed the two catalyst systems used.

Sample Preparation

Cyanate resins were blended with the catalytic system (360 ppm by weight of $Co(AcAc)_2$ or $Cu(AcAc)_2$ + 2% of the total resin weight of nonylphenol) prior to cure, and the blend was stored in the refrigerator in a desiccator to avoid moisture absorption. We have previously reported[11] that this amount of catalyst reduces the maximum temperature of the cure exotherm giving a higher reaction rate, which minimizes losses of volatility of the resin and increases the T_g of the cured material. The mixing procedure was as follows: The metal catalyst was dissolved in the co-catalyst NP at 100°C with continuous stirring until a homogeneous mixture was obtained, and cooled to room temperature. The catalytic blend was added to the preselected weight of the molten cyanate resin at 90°C, stirred for 5 min to obtain a homogeneous mixture, and immediately quenched before any reaction could occur.

A set of tubes containing about 30 mg of each sample was placed in an oil bath at the curing temperature (between 130°C and 220°C). Tubes were extracted from the bath at different times, the reaction was quenched by rapid cooling in an ice bath, and THF was added to produce a 1% (w/v) solution, which was injected into the chromatograph. The first appearance of an insoluble fraction showed that gelation had been attained.

Kinetic Characterization

The polymerization kinetics up to gelation were followed by SEC of the partially reacted samples at a selected curing temperature T_c ($T_c = 160°$, 180°, 190°, 200°, and 220°C for the uncatalyzed system; $T_c = 140°$, 150°, 160°, 170°, and 180°C for the cobalt catalyzed system; and $T_c = 130°$, 140°, 150°, and 160°C for the copper catalyzed system) with and without catalyst. The liquid chromatograph consisted of a model 590 solvent-delivery system and a U6K universal injector from Waters (Milford, MA, USA). Detection was carried out with a Kontron ultraviolet detector at $\lambda = 254$ nm and a refractive index detector model 2410 from Waters. Refractive index data collection and handling were carried out using the Millennium[32] Chromatography Manager from Waters. The system was equipped with μ-Styragel columns (30 cm length × 0.78 cm i.d.) packed with highly

cross-linked styrene-divinylbenzene copolymer of 10^3 and 100 Å nominal pore size from Waters. Polystyrene standards were used for the column calibration. Chromatograms were obtained at a flow rate of 1.0 mL min^{-1} by injection of 100 μL of 1.0% (w/v) solute solutions prepared using THF as solvent.

The kinetics in the pregel stage can be determined by following the decrease with time in the area of AroCy B10 peak in the chromatograms. The overall conversion of dicyanate groups by assuming equal reactivity of the cyanate groups and that there are no substitution effects is given by[14]: $x = 1 - (A/A_0)^{1/2}$, where A/A_0 is the ratio of the peak area at any time with respect to the initial peak area. Gelation was noticed during sample preparation before injection. The corresponding gel-point conversion was determined from the residual monomer peak.

Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer DSC-7 supported by a personal computer running DSC7 software kit (version 3.1) for data acquisition. The DSC was calibrated with high purity indium and zinc. Samples of 8 to 10 mg were weighed into 50 μL DSC aluminium pans, and experiments were conducted under a nitrogen flow of 20 mL min^{-1}. Isothermal curing was carried out at different curing temperatures ($T_c = 160°, 180°, 190°, 200°$, and $220°C$ for the uncatalyzed system; $T_c = 140°, 150°, 160°, 170°$, and $180°C$ for the cobalt catalyzed system; and $T_c = 130°, 140°, 150°$, and $160°C$ for the copper catalyzed system). After these experiments the samples were quenched to room temperature. All samples were then subjected to a dynamic DSC scan from $30°$ to $380°C$ at $10°C/min$ to determine the residual heat of reaction ΔH_{res} and the glass transition temperature T_g of the cured material. The residual heat of reaction was calculated from the exothermic peak by integrating the area between the heat flow curve and the baseline.

The conversion of each sample under isothermal conditions by assuming a single reaction mechanism can be calculated by $x = \frac{(\Delta H_{iso})_t}{\Delta H_{iso} + \Delta H_{res}}$, where $(\Delta H_{iso})_t$ is the heat of reaction at a time t calculated from the isothermal mode, and $(\Delta H_{iso} + \Delta H_{res})$ is the total heat of reaction obtained from the addition of the total heat from the isothermal mode ΔH_{iso} to the residual one. The accuracy of the values $(\Delta H_{iso} + \Delta H_{res})$ is ± 10 J/g with respect the polymerization enthalpies, ΔH_{tot}, calculated from dynamic scans at $10°C/min$ ($\Delta H_{tot} = 710 \pm 10$ J/g) for AroCy B10, in agreement with literature data[1].

RESULTS AND DISCUSSION

The determination of the cyanate conversion by size exclusion chromatography is based on the measurement of the area of the dicyanate monomer peak in the elution profile and relies on the fact that

the monomer concentration can be linearly correlated with the area of the generated peak. The catalyst is normally used for industrial purposes because trimerization rates of uncatalyzed dicyanates are slow and are a function of the concentration of active hydrogen impurities. This reaction is normally catalyzed by a mixture of metal cations and an active hydrogen initiator, such as nonylphenol. In this regard, Figure 1a shows the refractive index (RI) and UV detector response on injection of diverse AroCy B10 solutions with concentrations ranging from 0.001 to 0.15 g/mL (chromatograms from bottom to top). The dicyanate monomer shows a single peak at an elution volume, $V_e = (17.3 \pm 0.1)$ mL. This indicates that no polymerization reaction has taken place and that we are dealing with a high purity monomer. The area of the peaks obtained from the RI and UV detectors shows good linear dependence with AroCy B10 concentration (see Figure 1b), and can be used as calibration graphs to study the disappearance of the dicyanate monomer during polymerization. In relation with the catalyzed systems, the catalyst mixture alone (Co/NP or Cu/NP) elutes at (17.4 ± 0.1) mL, similarly to the monomer peak. However, at the concentrations used, the area of this peak is negligible, the catalyst is assumed not to react, and the disappearance of the monomer peak can be attributed to the dicyanate polymerization. For the systems (AroCy B10 + Co/NP) and (AroCy B10 + Cu/NP) calibration curves have been also obtained. The chromatograms depict a single peak at
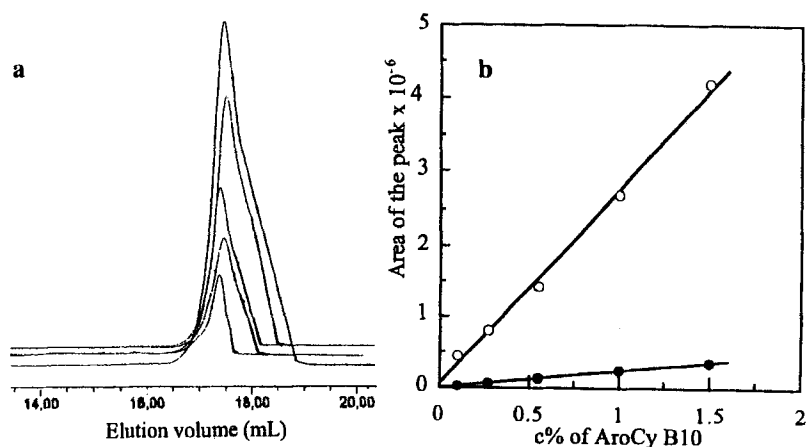

FIGURE 1 (a) Elution profiles for 100 μL of Arocy B10 at different concentrations in %(w/v). Eluent: THF; RI detector; (b) Area of the Arocy B10 peaks against the injected monomer concentration, (O) RI detector and (●) UV detector.

$V_e = (17.3 \pm 0.1)$ mL, and a linear relationship between area of the peak and system concentration similar to Figure 1b was obtained.

Curing the cyanate resin under isothermal conditions consumes monomer, and, therefore, SEC can be used to follow the monomer conversion; higher molar mass species will appear that could be detected in the chromatogram at different reaction times. As an example, the RI detector response during polymerization is shown in Figure 2. Figure 2a displays the chromatograms of the uncatalyzed samples in the pre-gel state at different reaction times cured at $T_c = 180°C$ and Figure 2b of the cobalt catalyzed sample at $T_c = 160°C$. The peaks from right to left were identified (based on the corresponding calculated molar mass versus elution times calibration) as monomer at an elution volume of 17.3 mL and the 3-mer appearing around 15.9 mL. One small peak appeared on the right of the trimer peak and can be attributed to side products and/or reaction intermediates (such as a dimer) at retention times between those of the monomer and trimer[10]. The other one on the left might be due to the formation of five-membered oligomeric species.

On the basis of these chromatograms, it is clearly evident that trimerization is the dominant reaction pathway (approx. 90%), as has been previously reported[8]. It is not the intention of this work to make an absolute assignment of the peaks observed. As the cure proceeds,
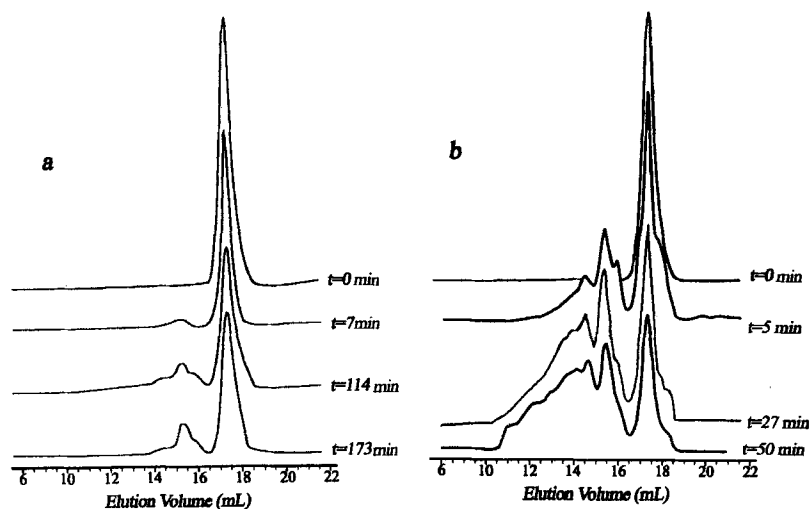
FIGURE 2 Elution profiles at 1 mL/min during the cure of AroCy B10: (a) neat resin at 180°C; (b) cobalt catalyzed resin at 160°C.

reactions between the growing chain and with the monomer result in a wide range of oligomeric species. The overall species distribution becomes broader as the system approaches gelation, as evidenced by the lower chromatogram at approximately 0.55–0.60% conversion. Although both RI and UV detectors can be used to follow the dicyanate conversion giving similar results, in this paper the conversion plotted is specifically obtained from the RI response due to the ease of handling the measurements. Moreover, in order to clarify the network buildup, the chromatogram of AroCy B10 at 30% conversion was compared with the one obtained from 1% THF solution of the commercial product AroCy B30, which is assumed to have yielded the same conversion. Under the experimental conditions used, AroCy B30 shows four distinct peaks at $V_e = 17.3$, 15.9, 15.3, 14.5, and 13.8 mL. The one at 17.3 mL corresponds to the monomer, 15.3 mL to the 3-mer, 14.5 mL to the 5-mer, and 13.8 mL to the 7-mer. (The first step in the buildup of the network is the formation of trimer and species identifiable in increments of two monomers up to seven monomers). From the areas of neat AroCy B10 and the peak of AroCy B30 that elutes at 17.3 mL, a conversion of 30% of cyanate groups is observed.
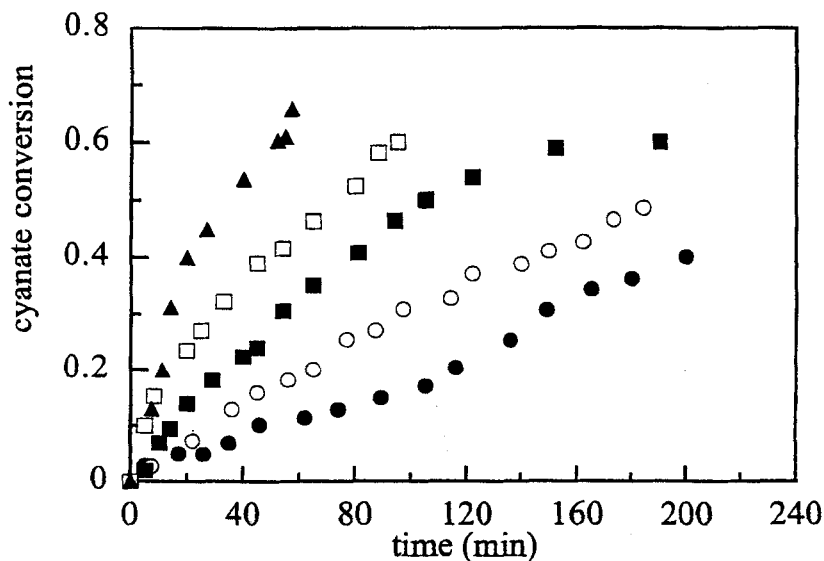
FIGURE 3 Conversion of cyanate groups as a function of time for the curing a neat AroCy B10 at different temperatures: (●) 160°C; (○) 180°C; (■) 190°C; (□) 200°C; and (▲) 220°C.

The evolution of uncatalyzed dicyanate conversion with time at different curing temperatures is depicted in Figure 3. At $T_c = 160°C$ the reaction is relatively slow and no conversion higher than 40% is attained after a curing time of 240 min. Increasing the cure temperature up to 220°C accelerates the reaction reaching conversions of 60% in approximately 55 min.

The catalyzed cyanate conversions as a function of the curing temperature are shown in Figures 4 and 5 for the cobalt and copper catalyzed systems, respectively. Comparison of these figures indicates that the reaction rate increases in the presence of copper catalyst.

Figure 6 depicts good reproducibility of the SEC technique for the cobalt catalyzed system at $T_c = 160°C$. To test the accuracy of this technique, in the same figure conversion data obtained from DSC are compared with size exclusion chromatography data at $T_c = 140°C$ as an example, showing good accord. Similar results have been obtained for other curing temperatures.

The experimental cyanate conversions plotted in Figures 3 to 5 were well fitted with a second-order kinetic expression with respect to the disappearance of monomer, that is $\frac{dx}{dt} = k(1 - x)^2$, in agreement with literature data[7,13,15] where the rate of the reaction is also kinetically controlled. No autocatalytic character could be attributed to this
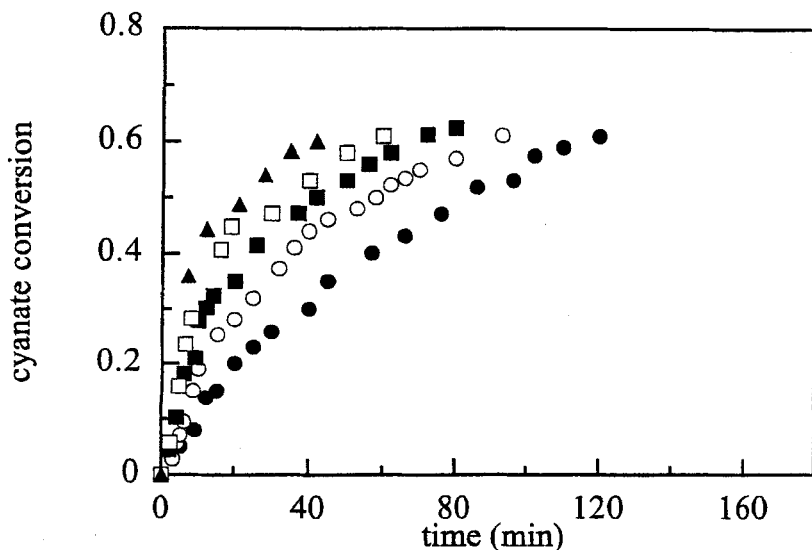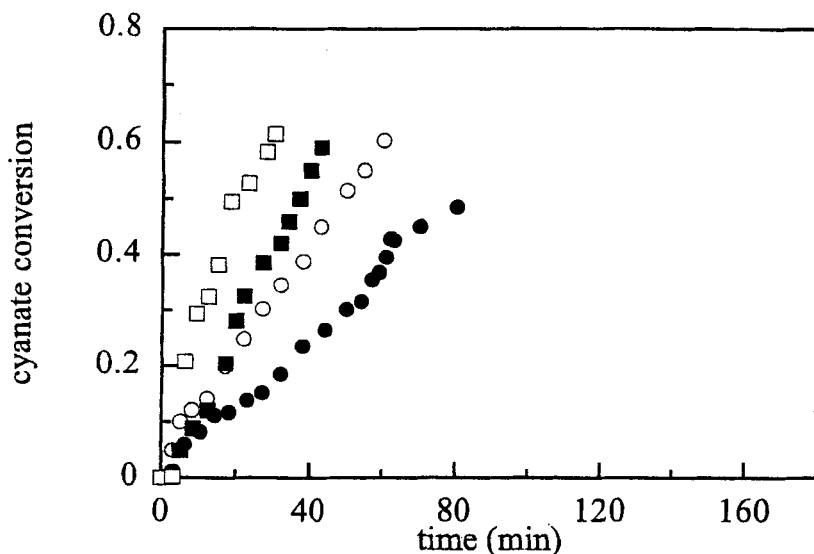

FIGURE 4 Cyanate conversion profiles for the cobalt catalyzed resin at different temperatures: (●) 140°C; (○) 150°C; (■) 160°C; (□) 170°C; and (▲) 180°C.

I. B. Recalde et al.

FIGURE 5 Cyanate conversion profiles for the copper catalyzed resin at different temperatures: (●) 130°C; (○) 140°C; (■) 150°C; and (□) 160°C.

reaction. A linear fit of ln(apparent rate constant) as a function of 1/(cure temperature) is attained giving activation energies of 70.1, 69.0, and 72 kJ/mol for the uncatalyzed, the cobalt catalyzed, and the copper catalyzed systems, respectively, in agreement with previous studies[7,11,16].

Monitoring the cure behavior of these systems includes the determination of the gel time t_{gel}, times for which one observes the appearance of insoluble particles indicating that a tridimensional network has been formed, as well as the corresponding conversion degrees x_{gel}. Gelation times t_{gel} show a linear plot of ln(t_{gel}) as a function of $1/T_c$ with activation energies of 77, 70.1, and 77 kJ/mol for the uncatalyzed, the cobalt catalyzed, and the copper catalyzed systems, respectively. The determined cyanate conversions at gelation x_{gel} were in the range 0.58–0.62, slightly higher than the mean-field predictions but in the same order as most of the published results[8,10,16–18]. The deviation of the experimental gel conversions from the mean-field value has been previously discussed[2,8,10,19]. In general, all systems are expected to have some deviations because of the assumptions of the mean-field theory. In the present systems, factors such as an intramolecular cyclization effect, the formation of side products[2], or the effects of moisture in the air[19] could contribute to delay gelation.
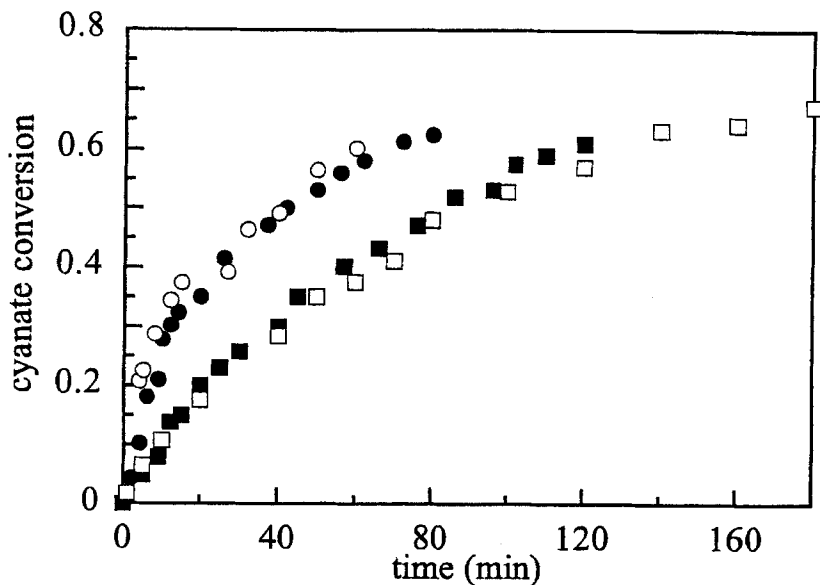
FIGURE 6 Experimental conversion versus curing time for the cobalt catalyzed resin showing comparison of dicyanate conversion obtained by SEC (■) and DSC (□) at 140°C and reproducibility of the SEC measurements at 160°C (● and ○).

CONCLUSION

The kinetics of uncatalyzed, cobalt catalyzed, and copper catalyzed AroCy B10, expressed as conversion of cyanate groups as a function of time, have been determined up to the gel point by size exclusion chromatography at different isothermal temperatures by using the disappearance of the dicyanate monomer peak in the chromatograms. The technique shows good reproducibility and accuracy with data obtained from differential scanning calorimetry. The reaction proceeds faster in the presence of the copper catalyst. A second-order rate equation fits well with the experimental data in this kinetically controlled regime. The activation energies obtained from the kinetic equation and from the time to gelation agree with literature data.

ACKNOWLEDGMENTS

REFERENCES

[1] *Chemistry and Technology of Cyanate Ester Resins*, Hamerton, I., Ed., Blackie Academic and Professional, Glasgow, 1994.

[2] T. Fang and D. A. Shimp (1995). *Prog. Polym. Sci.*, **20**, 61.

[3] J. Bauer, M. Bauer, and H. Much (1987). *Acta Polym.*, **19**, 221.

[4] M. Bauer, J. Bauer, and B. Garske (1986). *Acta Polym.*, **37**, 604.

[5] M. Bauer, J. Bauer, and G. Kühn (1986). *Acta Polym.*, **37**, 715.

[6] V. V. Korshak, V. A. Pankratov, A. A. Ladovskaya, and S. V. Vinogradova (1978). *J. Polym. Sci. Chem.*, **16**, 1697.

[7] A. Osei-Owusu, G. C. Martin, and J. T. Gotro (1992). *Polym. Eng. Sci.*, **32**, 535.

[8] A. M. Gupta and C. W. Makosko (1993). *Macromolecules*, **26**, 2455.

[9] Y.-H. Wang, Y.-L. Hong, and J. L. Hong (1995). *J. Appl. Polym. Sci.*, **58**, 1585.

[10] L. J. Kasehagen and C. W. Macosko (1997). *Polym. Int.*, **44**, 237.

[11] I. Harismendy, C. Gómez, M. Ormaetxea, M. D. Martín, A. Eceiza, and I. Mondragon (1997). *J. Polym. Mater.*, **14**, 317.

[12] I. Harismendy, M. Del Río, A. Eceiza, J. Gavalda, C. M. Gómez, and I. Mondragon (2000). *J. Appl. Polym. Sci.*, **76**, 1037.

[13] I. Harismendy, C. M. Gómez, M. Del Río, and I. Mondragon (2000). *Polym. Int.*, **49**, 735.

[14] D. Verchére, H. Sautereau, J. P. Pascault, C. C. Ricardi, S. M. Moschiar, and R. J. J. Williams (1990). *Macromolecules*, **23**, 725.

[15] H. Liu and G. A. George (1996). *Polymer*, **37**, 3675.

[16] Y. Den and G. C. Martin (1996). *Polymer*, **37**, 3593.

[17] Y. T. Chen and C. W. Macosko (1996). *J. Appl. Polym. Sci.*, **62**, 567.

[18] A. K. Bonetskaya, V. V. Ivanov, M. A. Kravchenko, V. A. Pankratov, T. M. Frenkel, V. V. Korshak, and S. V. Vinogradova (1980). *Polym. Sci. USSR*, **22**, 845.

[19] O. Georjon, J. Galy, and J. P. Pascault (1993). *J. Appl. Polym. Sci.*, **49**, 1441.