Polyurethane Macroazoinitiators Based on 2,2'-Azobis(2-cyanopropanol) Kinetic Studies

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SYNOPSIS

2,2'-Azobis(2-cyanopropanol) (ACP) was used to react with 4,4'-methylene diphenyl diisocyanate (MDI) and α,ω-hydroxy polycaprolactone (PCL) in the presence of dibutyltin dilaurate (SnDBDL) as a catalyst in a two-stage polycondensation to produce a polyurethane macroazoinitiator (PUMAI). The kinetics of the reaction of ACP with a monoisocyanate (para-tolylisocyanate, p-TI) was followed using high performance liquid chromatography. The condensation reaction was performed in 2-butanone, with SnDBDL as catalyst. Kinetic models were suggested to calculate rate constants. The experimental results showed an autocatalytic effect of the reaction by urethane groups and a different reactivity of the second OH group of ACP after the reaction of the first one. The kinetics of the reaction of MDI with ACP and PCL were studied using size exclusion chromatography. Polycondensation was performed under the same conditions used for the model system. The reaction rates of MDI with ACP and PCL were compared. ACP was shown to be slightly more reactive with MDI than PCL. The first stage of PUMAI synthesis (reaction of ACP with a large excess of MDI) was studied. Some side reactions with isocyanates occured. Finally, a typical PUMAI was synthesized. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Block copolymers are used intensively as thermoplastic elastomers, modifiers for polymers, or compatibilizer for polymer blends. Most of these block copolymers are prepared by anionic or cationic polymerization. These methods are not available for all kinds of monomers. In addition, these techniques are sensitive to impurities such as moisture or oxygen. The synthesis of block copolymers using different propagating species allows multiple combinations of monomers. Recently several kinds of block copolymers have been prepared using macroazoinitiators (MAI). MAIs are synthesized using materials having both polycondensation functions[1,2] or ionic initiation ability[3,4] and radical initiation species. Many studies have focused on the preparation of different block copolymers using different kinds of MAIs. Different polyurethane macroazoinitiators (PUMAI) have been synthesized.[5,6,7] More recently Shimura and Chen[8] have studied the thermodegradable properties of polyurethane macroazoinitiators (PUMAI) synthesized using 2,2'-azobis(2-cyanopropanol) (ACP), α,ω-hydroxy polycaprolactone (PCL; $\overline{M_n}$ = 2000 g/mol), and 4,4'-methylene diphenyl diisocyanate (MDI) in a two-stage polycondensation.

The mechanism of isocyanate–alcohol reactions depends on factors such as temperature, the ratio of monomers, the use of solvent, and the presence of a catalyst. Usually, the reaction rate of the first NCO is higher than the second one. In the case of MDI, it is known that, in toluene at 30°C with a triethylamine catalyst, the reactivity ratio of the substituted NCO to the initial one is $n = k_2/k_1$ = 0.66 (where k_1 and k_2, respectively, are the reaction rates of the initial and substitute NCOs with an excess of ethanol[9] or 1-butanol[10] (for equal reactivity, $k_2/k_1 = 1$).

The aim of this work is the control of the synthesis of various PUMAI. Paratolylisocyanate (p-TI) is used to simulate the reaction of ACP with MDI. First, a kinetic analysis was carried out by high performance liquid chromatography (HPLC). A kinetic model was suggested to calculate the reactivity ratio of the two ACP hydroxyl groups. Kinetic analysis of the reaction of MDI with ACP and PCL ($\overline{M_n} = 1000$ g/mol) was then carried out using size exclusion chromatography (SEC). Finally, the reactivity of ACP was compared to that of PCL when reacted with MDI. Besides the addition of hydroxyl groups to isocyanate groups giving the formation of urethane groups ($-$NHCOO$-$), the formation of allophanate and biuret groups and the reaction between isocyanate and water can take place. In the present paper, Fourier transform infrared spectroscopy (FT IR) was used for the determination of different groups formed when a large excess of diisocyanate (MDI) reacts with dihydroxyl (ACP) in 2-butanone solvent. The thermal decomposition of ACP, the reaction product of ACP with p-TI and MDI, and PUMAIs will be published later.

EXPERIMENTAL

Materials

4,4'-Methylene diphenyl diisocyanate (MDI) (Bayer), and para-tolylisocyanate (p-TI) (Aldrich) (Table I) were used without further purification. α,ω-hydroxy polycaprolactone (PCL; $\overline{M_n} = 1000$ g/mol) (Interox Chemical) was dried under reduced pressure for 3 h at 100°C before use. 2,2'-azobis(2-cyanopropanol)

(ACP) (Wako Chemicals) was washed by swirling in diethyl ether for 3 h at 25°C, then filtered, and finally dried under reduced pressure for two days. Dibutyltin dilaurate (SnDBDL), 2-butanone anhydrous, dibutylamine (DBA), and ortho-terphenyl (o-TP) were used as received.

Apparatuses

Fourier Transform Infrared (FTIR) Spectroscopy

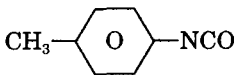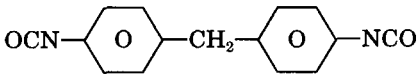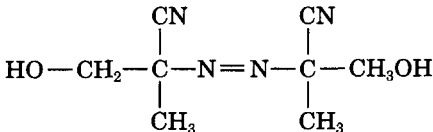FTIR analysis were carried out with a Magna-IR 550 spectrometer.

Proton Nuclear Magnetic Resonance (^{1}HNMR)

A Bruker AC200 was used with tetramethyl silane (TMS) as an internal standard. Analysis were carried out using deuterated acetone as solvent.

Size Exclusion Chromatography

SEC was performed using a Waters chromatograph equipped with a 510 pump, a U6K injector, and a double detection (484UV detector set at $\lambda = 254$ nm, and the differential refractometer R410). Tetrahydrofuran (THF) was used as an eluent solvent, and separation was carried out in two microstyragel columns (500 and 100 Å) with an elution rate of 1 mL/min. Peak heights were calculated using the differential refractometer detector. The average molar masses of PUMAIs ($\overline{M_n}$, $\overline{M_w}$), were determined by SEC using a Waters chromatograph with a 6000A pump, a U6K injector, and a double detection (UV at $\lambda = 254$ nm, and the differential refractometer R401). THF was used as an eluent, and the sepa-

Table I Raw Materials Employed to Prepare PUMAI and To Carry Out Kinetic Studies

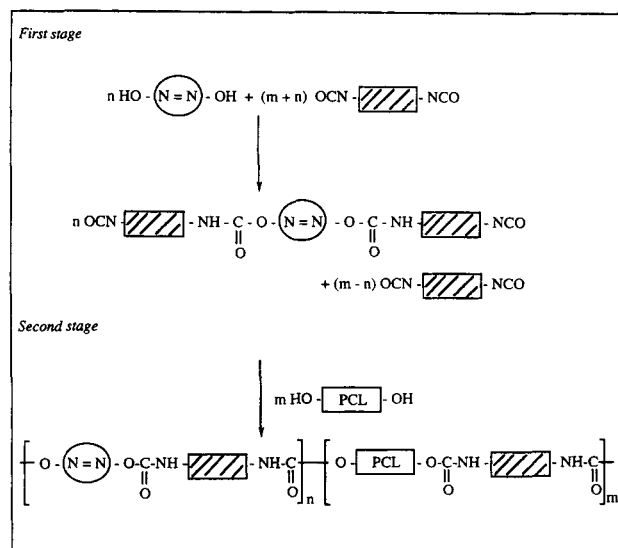| Designation	Chemical Formula	Molar Mass (g/mol)
p-TI	CH$_3$—⟨O⟩—NCO	133.15
MDI	OCN—⟨O⟩—CH$_2$—⟨O⟩—NCO	250
ACP	HO—CH$_2$—C(CN)(CH$_3$)—N=N—C(CN)(CH$_3$)—CH$_3$OH	196
PCL	H$\left[\text{O}\left[(CH_2)_5CO\right]_n O\right]_2$R	1000

ration was carried out in four microstyragel columns $(10^5, 10^4, 10^3,$ and 500 Å). The molar mass calibration curve was obtained using polystyrene standards.

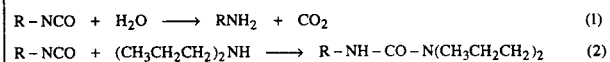### High Performance Liquid Chromatography

A Waters instrument was used with a low pressure gradient, a 600E solvent programmer, a U6K injector, and a UV486 detector set at 254 nm with a Nova pack C18 column (4 μ). The eluent was a mixture of double-filtered water (A) and acetonitrile (B) for UV spectroscopy. Peak heights were calculated using the UV detector. The chromatographic separations were achieved by using a gradient program. First, a gradient elution was carried out from 60 to 100 vol % acetonitrile (B) up to 10 min, then isocratic elution followed up to 18 min, after which a gradient elution was effected from 100 to 60 vol % (B) up to 30 min. The flow rate was 1 mL/min, and temperature was 20°C. 10 mL of the sample solution (0.2 wt % in acetonitrile) were injected. The internal standard was ortho-terphenyl.

Reaction Procedure of PUMAI Synthesis in Solution

A two-stage reaction procedure was used. The first stage involves the reaction of ACP with a large excess of MDI to form an NCO-terminated radical initiator without chain extension (due to the large excess of MDI). The reaction was carried out in solution (2-butanone) at 25°C for 3 h using SnDBDL as catalyst in a nitrogen atmosphere. In the second stage, the NCO-terminated radical initiator was chain extended with PCL ($\overline{M_n}$ = 1000 g/mol). The

Scheme 1 Synthesis of PUMAI.

$$R-NCO + H_2O \longrightarrow RNH_2 + CO_2 \qquad (1)$$
$$R-NCO + (CH_3CH_2CH_2)_2NH \longrightarrow R-NH-CO-N(CH_3CH_2CH_2)_2 \qquad (2)$$

Scheme 2 Isocyanate reaction with water and DBA.

stoichiometric mixture ([NCO]/[OH] = 1) was reacted 24 h at 35°C under nitrogen with stirring (Scheme 1).

Kinetic Reactions in Solution

The reactions of diols with monoisocyanate or diisocyanate were carried out in a glass reactor equipped with a mechanical stirrer, a reflux condenser protected by calcium chloride, and a nitrogen inlet tube.

ACP (0.49 or 0.98 g) or PCL (2.505 or 5.01 g) and orthoterphenyl (o-TP) (0.5 g) previously dissolved in 2-butanone (55 mL) were introduced into the reactor, which was placed in a thermoregulated oil bath at 35°C. O-TP is nonreactive and is used as an internal standard to quantify the concentration of monomers. After 20 min, a solution of p-TI (1.33 g) or MDI (1.25 g) in 2-butanone (40 mL) at the same temperature was added. SnDBDL ([SnDBDL]/ [NCO] = 0.05; mole fraction) was dissolved in 2-butanone (5 mL) and introduced into the reactor. A constant flow of nitrogen was maintained during the reaction. Samples were pipetted at regular intervals.

The kinetic reaction of ACP with p-TI was carried out by HPLC. However, this technique needs a stopping agent because residual NCO can react with the eluent (water) (Scheme 2). The samples were added to a large excess of dibutylamine. The reactivity of residual NCO groups is thus stopped, yielding urea (Scheme 2). Kinetic reactions of MDI with ACP or PCL were carried out by SEC. The samples were cooled in liquid nitrogen before SEC analysis.

RESULTS AND DISCUSSION

Models for Kinetic Studies

ACP contains two identical asymmetric centers and can therefore exist in meso and racemic forms. From an ^{1}H-NMR spectrum in acetone-d_6, we can assign two C-methyl singlets at 1.65 and 1.73 ppm (Fig. 1). It is assumed that both isomers have the same reactivity. Due to the symmetry of the ACP molecule, the reactivity of the two hydroxyl groups is also initially equivalent. The reaction between ACP and p-TI can be described by Scheme 3.

In the present work, we investigated whether the reaction of the initial hydroxyl group modifies the reactivity of the second due to electronic effects. The rates of the reactions between ACP and p-TI in 2-butanone at 35°C in the presence of SnDBDL were measured by HPLC. Figure 2 shows the HPLC chrotomatograms obtained at different reaction times for (NCO/OH = 0.5). All compound and reaction product elution times are listed in Table II.

The disappearance of monomers can be shown by

$$X_t = \frac{[AA]_t}{[AA]_0}; \quad Y_t = \frac{[I]_t}{[I]_0}$$

where $[AA]_t$ and $[I]_t$ are the concentration of ACP and p-TI (or NCO) respectively, during the reaction expressed in mol/kg. X_t and Y_t can be calculated from the heights of the peaks (1 and 3) on HPLC chromatograms. The disappearance of Y_t and the formation of reaction products versus time are shown in Figure 3, where $H_{(t)}$ is the peak height of p-TI and reaction products at time t, and $H_{(0)}$ is the peak height of p-TI at time $t = 0$.

The rate of the catalysed reactions using Sn-DBDL as a catalyst depends on the dissociation of the catalyst and the concentration of the complex formed (Scheme 4).

Four limiting cases were proposed by Richter and Macosko[11] for bulk reactions. In solution, the con-
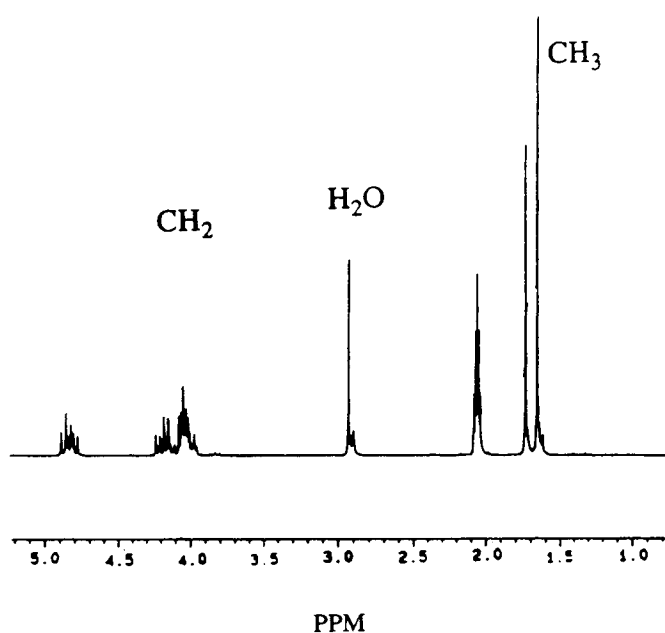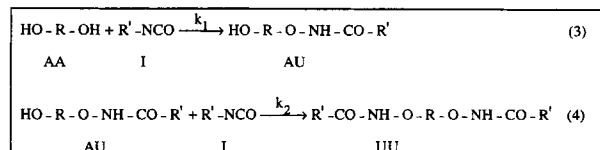
Scheme 3   Monoisocyanate reactions with diols.

centration of the complex (Sn^+I) is too low; therefore, two limiting cases are available (Table III). Assuming a dissociation mechanism of the catalyst [Case (a)], the reaction of ACP with p-TI can be described by Scheme 5.

$[AA]$, $[I]$, $[AU]$, and $[UU]$ are the molar concentrations of ACP, p-TI, monourethane (AU), and diurethane (UU), respectively. k_1 and k_2 are the reaction constants for the noncatalytic reaction rate of dihydroxyl (AA) and monourethane (AU) with an isocyanate, respectively. $k_{1c} = k_1 K_b [SnX]_0$ and $k_{2c} = k_2 K_b [SnX]_0$ are reaction constants for the catalysed reactions. The kinetic equations for reactions (8)–(11) (model 1) are as follows.

$$-\frac{d[AA]}{dt} = 2(k_1 + k_{1c})[I][AA] \quad (1)$$

$$-\frac{d[I]}{dt} = 2(k_1 + k_{1c})[I][AA]$$
$$+ (k_2 + k_{2c})[I][AU] \quad (2)$$

$$\frac{d[AU]}{dt} = -2(k_1 + k_{1c})[I][AA]$$
$$+ (k_2 + k_{2c})[I][AU] \quad (3)$$
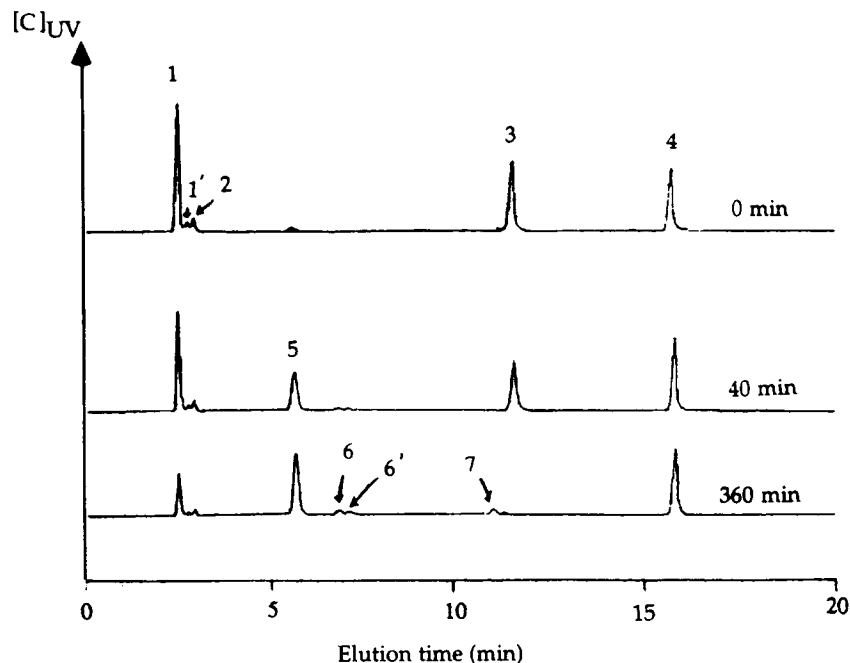
By denoting

$$k_1' = k_1 + k_{1c} \quad (4)$$

$$k_2' = k_2 + k_{2c} \quad (5)$$

$$X = \frac{[AA]}{[AA]_0}; \quad Y = \frac{[I]}{[I]_0}; \quad Z = \frac{[AU]}{[AA]_0} \quad (6)$$

$$K_1' = k_1'[AA]_0; \quad K_2' = k_2'[AA]_0 \quad (7)$$

$$r = \frac{[I]_0}{2[AA]_0} \quad (8)$$

The ratio of specific reaction rates λ is assumed to be constant and independent of temperature, as follows:

PPM

Figure 1 ^{1}HNMR spectrum of 2,2'azobis (2-cyanopropanol) (ACP) in acetone d_6.

Figure 2 Various HPLC chromatograms obtained during the reaction of ACP with p-TI (Solvent: 2-butanone. $T = 35°C$. Catalyst: $[SnDBDL] = 5.10^{-7}$ mol/L.)

$$K_2'/K_1' = k_2'/k_1' = \lambda \qquad (9)$$

The parameter λ gives the reactivity ratio of ACP once reacted (AU) to the initial hydroxyl (AA). The equal reactivity of hydroxy groups can be obtained

Table II Elution Time of Initial Compounds and Reaction Products Separated on Nova Pack C18 Column with Water and Acetonitrile as Eluent

Compound	Elution Time (min)
2,2'azobis (2-cyanopropanol)	
Isomer 1	2.95
Isomer 2	3.18
2-Butanone	3.4
p-TI-DBA	11.52
Ortho-terphenyl (o-TP)	15.53
Reaction Products	Elution Time (min)
ACP-p-TI	
Isomer 1,2	5.92
p-TI-ACP-p-TI	
Isomer 1	7.02
Isomer 2	7.28
Side reaction product (urea formation)	10.77

only when $\lambda = 1$. By introducing eqs. (4)–(9) in eqs. (1), (2), and (3), we obtain

$$-\frac{dX}{dt} = 4rK_1'XY \qquad (10)$$

$$-\frac{dY}{dt} = K_1'Y(2X + \lambda Z) \qquad (11)$$

$$\frac{dZ}{dt} = K_1'Y(-2X + \lambda Z) \qquad (12)$$

Neglecting eventual side products, we can then write,

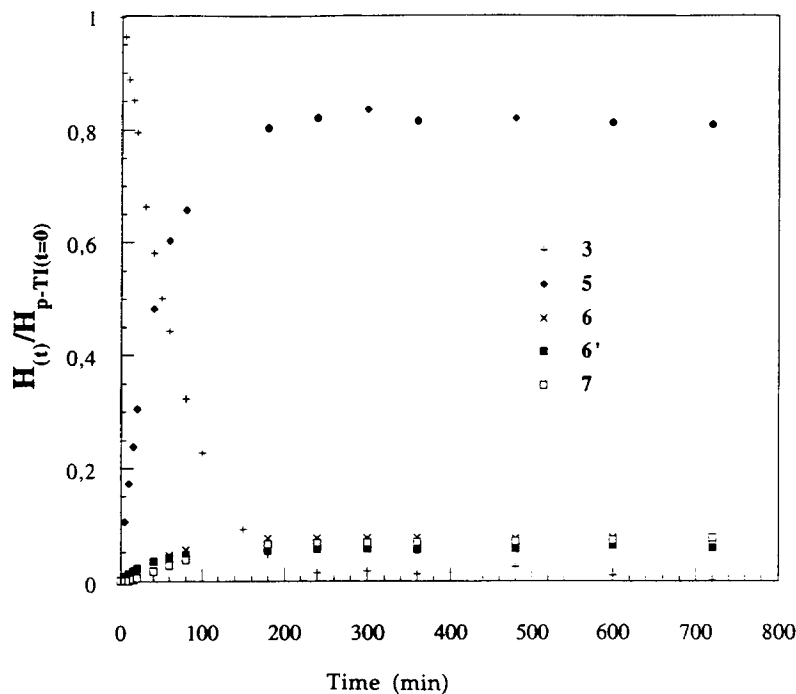$$[I]_0 - [I]_t = [A]_0 - [A]_t \qquad (13)$$

where

$$[A]_t = 2[AA]_t + [AU]_t \qquad (14)$$

and

$$[A]_0 = 2[AA]_0 \qquad (15)$$

By introducing eqs. (6), (8), (14), and (15) in eq. (13), we obtain

$$Z = 2[r(Y - 1)X + 1] \qquad (16)$$

Figure 3 p-TI disappearance and reaction products during the reaction of p-TI with ACP (Solvent: 2-butanone. $T = 35°C$. Catalyst: [SnDBDL] = 5.10^{-7} mol/l.) Symbols are as follows: (+), 3; (♦), 5; (×), 6; (■), 6'; (□), 7. (See also Table I and Figure 2.)
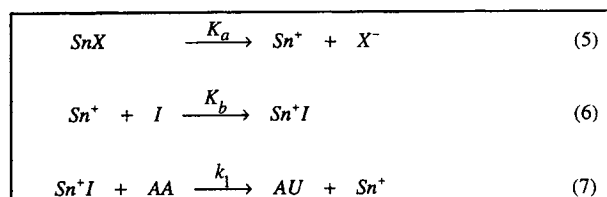
Equation (11) can then be written as follows:

$$\frac{dY}{dt} = -2K_1'Y[X + \lambda(r(Y - 1) + 1 - X)] \quad (17)$$

Dividing eq. (17) by eq. (10) leads to

$$\frac{dY}{dX} = \frac{1}{2r} + \frac{\lambda(Y - 1)}{2X} + \frac{(1 - X)\lambda}{2rX} \quad (18)$$

The relationship between X, Y, and λ may be obtained by integrating eq. (18). This leads to

$$Y = \frac{1 - \lambda}{(2 - \lambda)r} X - \frac{1 - r}{r} + \frac{1}{r(2 - \lambda)} X^{\lambda/2} \quad (19)$$

SnX $\xrightarrow{K_a}$ $Sn^+ + X^-$		(5)
$Sn^+ + I$ $\xrightarrow{K_b}$ Sn^+I		(6)
$Sn^+I + AA$ $\xrightarrow{k_1}$ $AU + Sn^+$		(7)

Scheme 4 Influence of SnDBDL on the reaction of isocyanate with hydroxy groups.

By defining $S = \lambda/2$, eq. (19) may then be written as follows:

$$2Yr + 2(1 - r) = \frac{1}{1 - S} (X^S - X) + 2X \quad (20)$$

At the end of the reaction with an excess of hydroxyl groups $(r < 1)$, all isocyanate groups have disappeared; therefore $Y = 0$. Equation (20) may then be written as follows:

$$2(1 - r) = \frac{1}{1 - S} (X^S - X) + 2X \quad (21)$$

This equation is similar to that found by Peebles[9] for the determination of the reactivity ratio of diisocyanate monomers. Knowing r and X values at the end of the reaction from HPLC ($T = 35°C$, [SnDBDL] = 5.10^{-6} mol/L), the parameter S and, subsequently λ, may be obtained by solving eq. (21). For $r = 0.5$ at the end of the reaction, $X = 0.285 \pm 0.005$; therefore, $S = 0.715 \pm 0.035$, and $\lambda = 1.43 \pm 0.07$.

The values λ, k_1', and k_2' (Table IV) are obtained by adjusting the kinetic model (integration of eqs. (10) and (17) using the Runge–Kutta numerical method) to experimental results (Fig. 4). The value

Table III   Limiting Cases Available for the Dissociation of DBTDL in 2-Butanone, K_a, K_b, and k_1

	Case (a)	Case (b)
Dissociation of SnX	high	low
$\dfrac{[Snx]}{[Sn^+] + [Sn^+I]}$	$\ll 1$	$\gg 1$
Concentration of complex	low	low
$\dfrac{[Sn^+]}{[Sn^+I]}$	$\gg 1$	$\gg 1$
Rate of urethane formation: $d[U]/dt$	$k_1 K_b [SnX]_0 [I][OH]$	$k_1 K_a^{0.5} K_b [SnX]_0^{0.5}[I][OH]$
k_{1c}	$k_1 K_b [SnX]_0$	$k_1 K_a^{0.5} K_b [SnX]_0^{0.5}$

See Scheme (5) (from Richter and Macosko[11]).

calculated using this method ($\lambda = 1.7$) is slightly higher than that found previously ($\lambda = 1.4$). The precision of the measurements is not very good; but both cases indicate that after the reaction of the first OH group, the second OH group of the ACP molecule is more reactive. Figure 4 shows that the kinetic model does not exactly match experimental data. Sato[12] suggested an autocatalytic effect by urethane groups for reactions between alcohol and isocyanate.

In addition to reactions (8)–(11), taking account the auto catalytic effect of urethane functions, the reaction between ACP and p-TI can be described in Scheme 5(c), where $[U]$ is the concentration of urethane groups and k_{1u} and k_{2u} are reaction constants for uncatalyzed and autocatalysed reactions [reactions (12) and (13)] (model 2).

The kinetic equations taking into account the nonautocatalytic effect [reactions (6)–(9)] and the

autocatalytic effect [reactions (10) and (11)] of urethane groups are as follows:

$$\frac{d[AA]}{dt} = -2(k_1 + k_{1c})[I][AA]$$

$$- 2k_{1u}[I][AA][U] \quad (22)$$

$$\frac{d[I]}{dt} = -2(k_1 + k_{1c})[I][AA] - (k_2 + k_{2c})[I][AU]$$

$$- 2k_{1u}[I][AA] + k_{2u}[I][AU][U] \quad (23)$$

By denoting

$$K_{1u} = k_{1u}[AA]_0[I]_0; \quad K_{2u} = k_{2u}[AA]_0[I]_0 \quad (24)$$

$$K_2'/K_1' = K_{2u}/K_{1u} = k_2'/k_1' = k_{2u}/k_{1u} = \lambda \quad (25)$$

The formation of urethane groups is equal to the disappearance of isocyanate functions [eq. (26)].
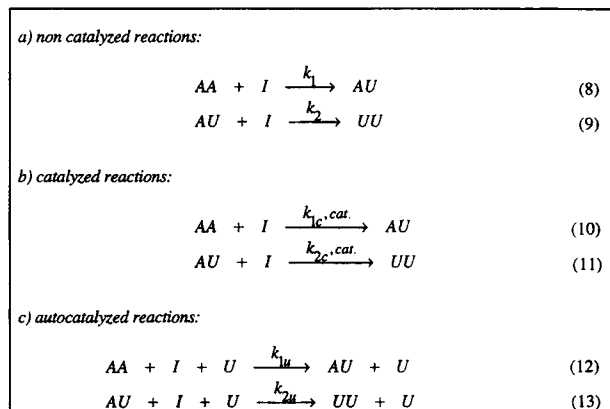
$$\frac{d[U]}{dt} = -\frac{d[I]}{dt} \quad (26)$$

By integrating eq. (26),

$$[U]_t = [I]_0 - [I]_t \quad (27)$$

Dividing eq. (27) by $[I]_0$ and using eq. (6), we can then write

$$[U]_t = (1 - Y)[I]_0 \quad (28)$$

a) non catalyzed reactions:

$$AA + I \xrightarrow{k_1} AU \quad (8)$$

$$AU + I \xrightarrow{k_2} UU \quad (9)$$

b) catalyzed reactions:

$$AA + I \xrightarrow{k_{1c}, cat.} AU \quad (10)$$

$$AU + I \xrightarrow{k_{2c}, cat.} UU \quad (11)$$

c) autocatalyzed reactions:

$$AA + I + U \xrightarrow{k_{1u}} AU + U \quad (12)$$

$$AU + I + U \xrightarrow{k_{2u}} UU + U \quad (13)$$

Scheme 5   Reactions of ACP with p-TI.

Table IV Values of k'_1, k'_2, k_{1u}, k_{2u}, and $\lambda = k'_2/k'_1 = k_{2u}/k_{1u}$ for the Reaction of ACP with p-TI Calculated Using Kinetic Models

Kinetic Model	k'_1 L mol^{-1} min^{-1}	k'_2 L mol^{-1} min^{-1}	k_{1u} L mol^{-2} min^{-2}	k_{2u} L mol^{-2} min^{-2}	$\lambda = k'_2/k'_1 = k_{2u}/k_{1u}$
Model 1	0.07	0.13	—	—	1.73
Model 2 (Auto Catalysed by Urethane Group)	0.05	0.08	0.94	1.53	1.63

2-butanone solution; $T = 35°C$; catalyst = SnDBDL.

Using eqs. (4)–(9), and eqs. (16), (24), (25), and (28), eqs. (22) and (23) may be written as follows:

$$-\frac{dX}{dt} = 4rXY[K'_1 + K_{1u}(1 - Y)] \qquad (29)$$

$$-\frac{dY}{dt} = 2Y[K'_1 + K_{1u}(1 - Y)]$$

$$\times [X + \lambda(r(Y - 1) + 1 - X)] \qquad (30)$$

The λ, k'_1, k'_2, k_{1u}, and k_{2u} values (Table IV) are obtained by adjusting the kinetic model [integration of eqs. (29) and (30) using the Runge–Kutta numerical method] to the experimental results. Figure 5 shows that the suggested kinetic model, taking into account the autocatalytic effect of the urethane group, fits very well with experimental data. The value of the specific reaction rate ratio ($\lambda = 1.6$) is not far from the previous calculation. It is interesting to note that k'_2 and k_{2u} are 1.6 times k'_1 and k_{1u}, respectively.
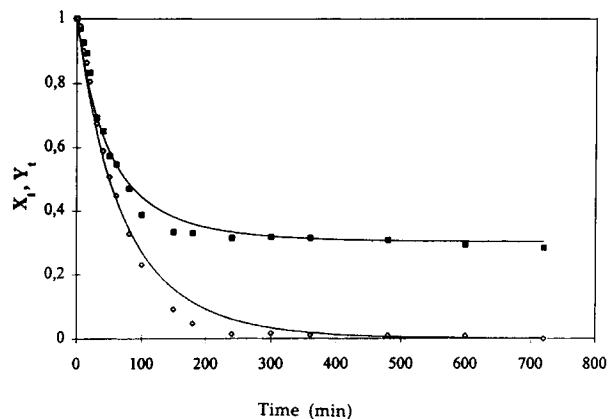
## KINETIC RESULTS FOR POLYURETHANE SYNTHESIS

Since it is known that the isocyanate groups in MDI are not equireactive and that ACP displays nonequireactive hydroxyl groups in our experimental conditions (2-butanone as solvent and SnDBDL as a catalyst), the analysis of the kinetic data of the reaction between ACP and MDI became more complicated. For these studies, 1 : 1 and 2 : 1 [NCO]/[OH] ratios were used. The reaction of MDI with ACP was compared with that of PCL ($\overline{M_n} = 1000$ g/mol) for 1 : 1 and 2 : 1 [NCO]/[OH] ratios.

Figure 6 shows the SEC chromatograms at different times for the reaction of MDI with ACP ($r = $ [NCO]/[OH] = 2). In the chromatogram at $t = 0$, the presence of a small peak at $t_e = 16.27$ min indicates that a part of the monomers had already reacted at the conventional starting time. At the end of the reaction, the presence of a small peak at the ACP elution time was noticed. This small peak

Figure 4 Decrease in the amount of remaining monomers during the reaction of ACP with p-TI. (Solvent: 2-butanone. $T = 35°C$. Catalyst: [SnDBDL] = 5.10^{-7} mol/L.) Solid line (——) represents simulation (model 1): ■ represents $X_t = [ACP]_t/[ACP]_0$; ◇ represents $Y_t = [p - TI]_t/[p - TI]_0$.

Figure 5 Decrease in the amount of remaining monomers during the polycondensation of ACP with p-TI. (Solvent: 2-butanone. $T = 35°C$. Catalyst: [SnDBDL] = 5.10^{-7} mol/L.) Solid line (——) represents simulation for autocatalysed reaction by urethane groups (model 2): ■ represents $X_t = [ACP]_t/[ACP]_0$; ◆ represents $Y_t = [p - TI]_t/[p - TI]_0$.
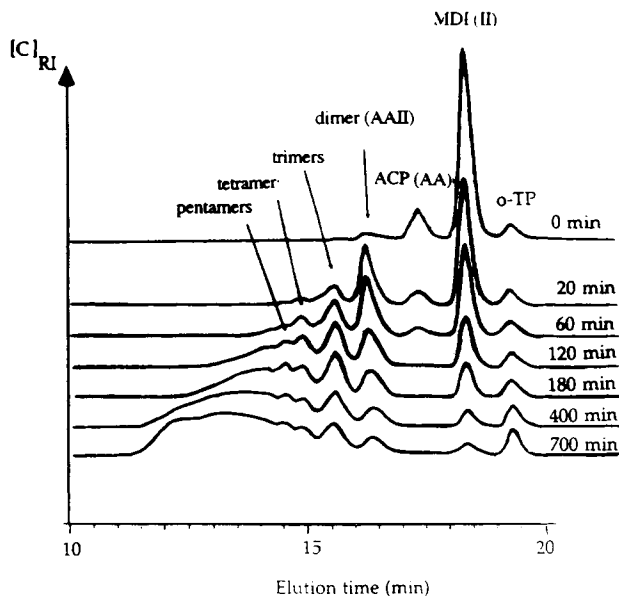
Figure 6 SEC chromatograms (UV detector) obtained during the reaction of ACP with MDI. (Solvent: 2-butanone. $T = 35°C$. Catalyst: [SnDBDL] $= 2,5.10^{-7}$ mol/L.) $r = [NCO]/[OH] = 2$.

is, in fact, due to the small amount of catalyst (SnDBDL) used in the reaction. For this reason, the real height of the ACP monomer is

$$h_t = \overline{h_t} - h_\infty \qquad (31)$$

where h_∞ is the height for the catalyst peak, $\overline{h_t}$ is the total height for ACP and the catalyst peak at time t, and h_t is the real height value for ACP at time t. Therefore, using the ACP and MDI calibration curves, we can determine the disappearance of the monomers in the following manner:

$$X_t = \frac{[ACP]_t}{[ACP]_0} = \frac{h_{ACP(t)}}{h_{ACP(t=0)}} \; ;$$

$$Y_t = \frac{[MDI]_t}{[MDI]_0} = \frac{h_{MDI(t)}}{h_{MDI(t=0)}} \qquad (32)$$

where $[ACP]$ and $[MDI]$ are the concentrations of the corresponding monomers expressed in mol/kg, and X_t and Y_t are calculated from the height of the peaks in SEC chromatograms.

Figure 7 shows the variation of X_t and Y_t over time at 35°C in 2-butanone with SnDBDL as a catalyst ([SnDBDL] $= 5.10^{-6}$ mol/L). Total conversion was reached after about 6 h. The residual MDI concentration was slightly higher than the ACP concentration. This is due to the substitution effect

Table V   Elution Time of Compounds and Reaction Products Obtained in SEC Chromatogram for the Reaction of ACP with MDI $r = [NCO]/[OH] = 10$

Compounds	Elution Time (min)
ACP or AA	17.49
MDI or II	18.44
Reaction Products	Elution Time (min)
AAII + urea	16.27
AAIIAA + AAIIAA	15.38
AAIIAAII	14.45
AAIIAAIIAA + IIAAIIAAII	13.93

of both monomers, positive in the case of ACP ($\lambda = 1.6$) and negative in the case of MDI ($n = 0.66$).[9,10]

Figure 8 shows the disappearance of MDI when it reacts with ACP and PCL ($\overline{M_n} = 1000$ g/mol) ($r = [NCO]/[OH] = 1$). The residual MDI concentration when reacted with ACP is slightly higher than that observed for the reaction of MDI with PCL. The same result was observed when $r = [NCO]/[OH] = 2$ (Fig. 9). Therefore, ACP is more reactive than PCL. This difference in reactivity may be explained by different electronic effects of the two molecules.

PUMAI SYNTHESIS

The first stage of PUMAI synthesis is the reaction of ACP (1 g) with a large excess of MDI (25.5 g)
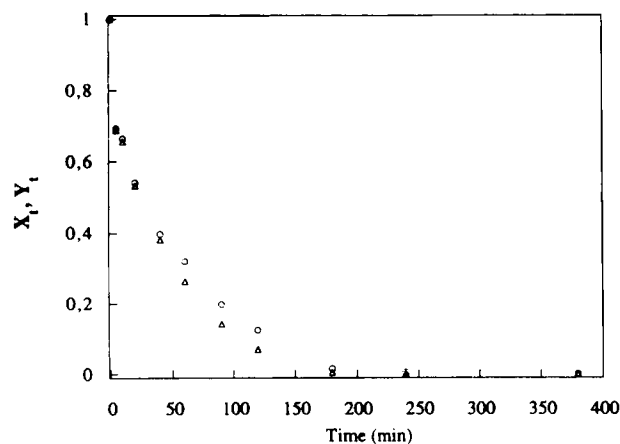
Figure 7 Monomer conversion during polycondensation of ACP with MDI. (Solvent: 2-butanone. $T = 35°C$. Catalyst: [SnDBDL] $= 5.10^{-7}$ mol/L.) $r = [NCO]/[OH] = 1$. O represents $X_t = [ACP]_t/[ACP]_0$; $\triangle$ represents $Y_t = [MDI]_t/[MDI]_0$.
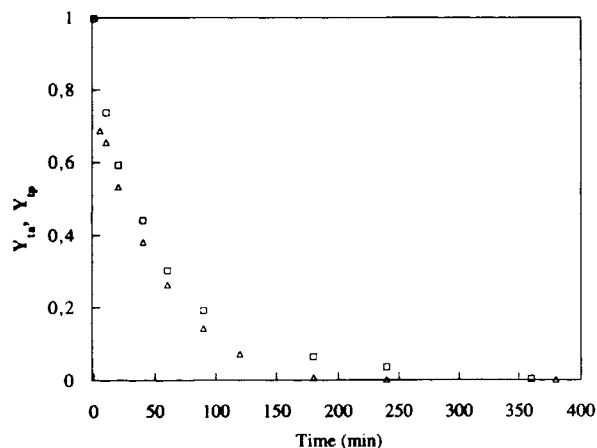
Figure 8 MDI conversion during polycondensation with ACP and PCL, respectively. (Solvent: 2-butanone. T = 35°C. Catalyst = SnDBDL.) r = [NCO]/[OH] = 1. △ represents Y_{ta} = $[MDI]_t/[MDI]_0$ (reacted with ACP); □ represents Y_{tp} = $[MDI]_t/[MDI]_0$ (reacted with PCL).
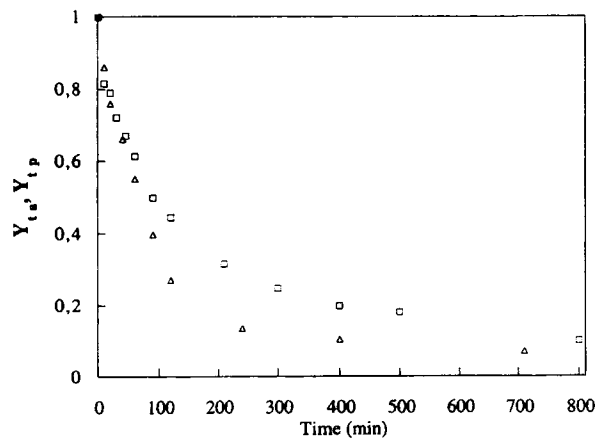
Figure 9 MDI conversion during polycondensation with ACP and PCL, respectively. (Solvent: 2-butanone. T = 35°C. Catalyst: [SnDBDL] = 5.10^{-7} mol/L.) r = [NCO]/[OH] = 2. △ represents Y_{ta} = $[MDI]_t/[MDI]_0$ (reacted with ACP); □ represents Y_{tp} = $[MDI]_t/[MDI]_0$ (reacted with PCL).

(in our case, r = [NCO]/[OH] = 20). The reaction occurs in (2-butanone) (260 g) at 25°C for 3 h with a catalyst (SnDBDL) (0.0644 g). Figure 10 shows the SEC chromatograms of ACP and MDI injected separately and their evolution over reaction time. Possible reaction products are listed in Table V. The peak at elution time 16.27 min could not be caused by the monourethane (AU) because, after three hours with a large excess of MDI and with catalyst, this peak would disappear. Therefore, we can assume that other species are due to side reactions, such as the dimerization of MDI or the reaction of NCO with water, yielding the formation of urea (Scheme 2). The peaks at 1643 and 3309 cm^{-1} on the FT IR spectrum corresponding to the absorption of C=O and NH urea, respectively, reveal the formation of urea groups (Fig. 11). Figure 10 shows the existence of a small amount of oligomers containing two azo groups: tetramer, $(AAII)_2$, and pentamer, $II(AAII)_2$. The first stage of PUMAI synthesis allows us to control the azo content by varying r values and, therefore, the number of azo groups in each of the PUMAI chains. In the second stage, the NCO-terminated radical initiator was chain extended with PCL (96.94 g) ($\overline{M_n}$ = 1000 g/mol), during 24 h at 35°C under nitrogen with stirring the overall stoechiometric ratio ([NCO]/[OH] = 1) was respected. The position of azo groups could be modified by changing the order of the two stages of PUMAIs synthesis.

The SEC chromatogram of a polyurethane macroazo initiator (PUMAI) is shown in Figure 12. The number average molar mass obtained is in the

range of 27,000 g/mol, and the mass average molar mass is in the range of 68,000 g/mol (polystyrène standards). The polydispersity is, therefore, close to 2.7. By heating in presence of vinyl monomers,
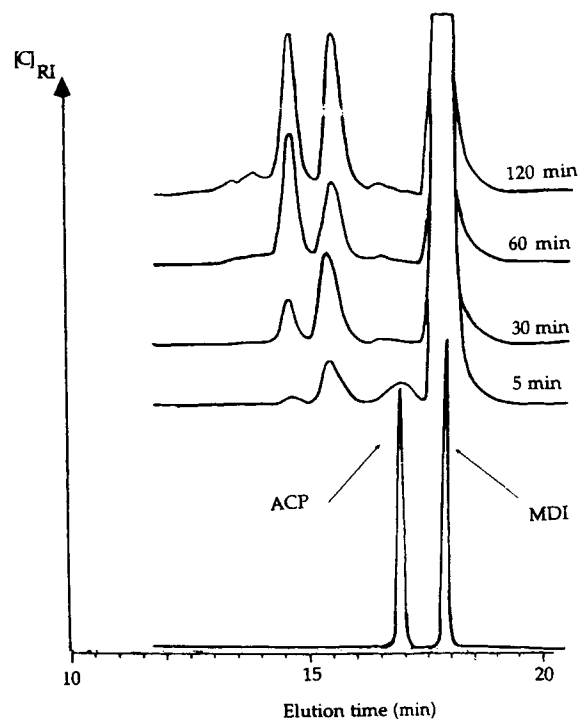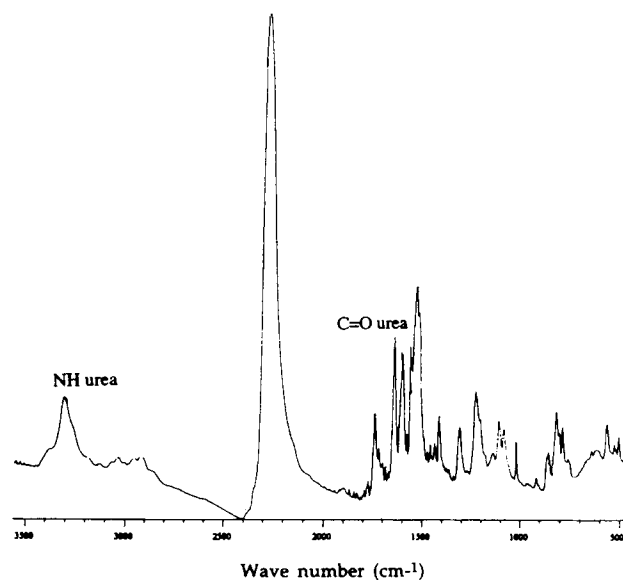

Figure 10 SEC chromatograms (RI detector) obtained during the reaction of ACP with MDI. (Solvent: 2-butanone. T = 35°C. Catalyst = SnDBDL.) r = [NCO]/[OH] = 10.

these PUMAIs are able to initiate radical polymerization. The position of azo groups in PUMAIs should have an influence on the type of the block copolymers synthesized.
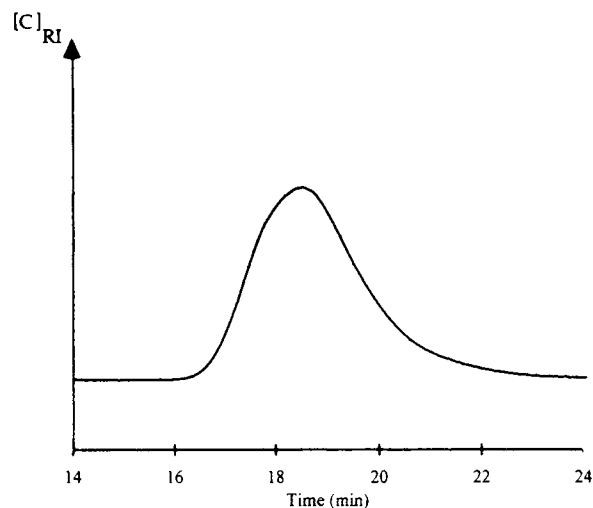
CONCLUSION

The unequal reactivity of the two hydroxyl groups of 2,2′-azobis(2-cyanopropanol) (ACP) towards isocyanate functions in the presence of a catalyst (dibutyltin dilaurate) was established by a kinetic study with a monofunctional aromatic isocyanate. The kinetics of the reaction also showed an autocatalytic effect by urethane group. The reactivity ratio of the substituted OH group to the initial one is 1.6. MDI is slightly more reactive with ACP than with PCL. When a large excess of MDI reacts with ACP (the first stage of PUMAIs synthesis), hydrolysis of some isocyanate groups occurred due to moisture.

The decomposition of PUMAIs and synthesis of block copolymers, as well as their characterization and applications, will be published later.

Figure 12   SEC chromatogram (RI detector) obtained for a typical PUMAI.

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Wave number (cm⁻¹)

Figure 11   FT IR spectrum of the product of the reaction of ACP with MDI. r = [NCO]/[OH] = 20.