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Kinetics of the Reaction between Polyester Acid and Carbodiimide in Dry Polyester Diols and in a Polyester Polyurethane

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ABSTRACT: The kinetics of reaction between mono- or polycarbodiimide and organic acid attached to polyester have been studied in dry polyester diols, in a polyester-based polyurethane elastomer, and in solution in tetrahydrofuran. Initial acid and carbodiimide contents were about 7×10^{-5} equiv/g. The monocarbodiimide is soluble in the three media, so its reactions are homogeneous. At 85 °C the range of second-order rate constants is 100–300 g/(equiv·min). The activation energy is 75 kJ/mol except in the elastomer, in which the value is 53 kJ/mol. The polycarbodiimide used is insoluble in polyester and in the elastomer, so its reactions in these media are heterogeneous. Nevertheless, the kinetics appear to be second order in the polyester diols. At 85 °C, rate constants for three different polyester diols are between 7 and 25 g/(equiv·min) and activation energies are between 95 and 138 kJ/mol. The apparent second-order rate constant in the elastomer decreases with time. At 85 °C the initial value is 12 g/(equiv·min) and the activation energy is 82 kJ/mol. The polycarbodiimide is soluble in tetrahydrofuran. At 85 °C the rate constant is 60 g/(equiv·min) and the activation energy is 80 kJ/mol. Thus rate constants are much the same in a mobile liquid, for polyesters of several viscosities, and in an elastomer.

Introduction

Hydrolytic degradation of polyester-based polyurethanes is due to the acid-catalyzed hydrolysis of the ester linkage.[1,2] Polyester diols used to make the polyurethanes have an acid content of about 10^{-5} equiv/g.[1] This is not changed by reaction with isocyanate during urethane formation and so is the acid source for the initial degradation.[1] Carbodiimides, which react with acids, have been used to increase the lifetimes of polyester-based polyurethanes in moist environments.[1,3,4] Consequently, the kinetics of the reaction between polyester acid and carbodiimide are of practical importance. Kinetic processes in a polymer have added interest because of the high viscosity of the medium. For this paper acid and carbodiimide contents were measured as functions of time and temperature during mutual reaction in dry polyester diols, in a dry thermoplastic polyurethane elastomer made from one diol, and in solution in tetrahydrofuran. The data were used to calculate rate constants in the different media.

Experimental Section

N,*N*-Dimethylformamide, stabilized tetrahydrofuran, bis[4-(isocyanato)phenyl]methane (commonly MDI (4,4′-diphenylmethane diisocyanate)), and α,ω-diols of poly(caprolactone) (CA registry 24980-41-4, hereafter PCL) of number-average molecular weights 530 and 2000 were purchased from commercial sources. An α,ω-diol of poly(1,4-butylene adipate) (CA registry 25103-87-1, hereafter PBA) of number-average molecular weight 930, with an unusually high acid content, and two carbodiimides, one monomeric (M) and one polymeric (P), were donated by companies active in the urethane field. M is a commercial grade of bis(2,6-diisopropylphenyl)carbodiimide. The exact structure of P is not known but such materials have been described as low polymers formed by reaction of sterically hindered diisocyanates or by exchange reaction between sterically hindered monocarbodiimides and hindered diisocyanates.[3] Consistent with this, infrared spectra of P indicated that it contained aliphatic groups and a highly substituted aromatic ring. The chromatogram of P on a gel permeation column showed several closely spaced peaks; the number-average molecular weight probably was about 600. Under a microscope, particles of P appeared irregularly shaped, ranging in average cross dimension from 0.03 mm to less than 0.001 mm. Many were about 0.005 mm across. At 65 °C, P softened to a viscous liquid.

The carbodiimide contents of M and P were determined by reacting known masses with excess oxalic acid in dry dioxane,[5] which had been degassed in three freeze–evacuate–thaw cycles, and slowly passing the carbon monoxide and carbon dioxide formed through two preevacuated cold traps, the first cooled with dry ice and the second with liquid nitrogen. After evacuation only the carbon dioxide remained in the second trap, from which it was transferred to a system of known volume, where its pressure was measured. The amount of carbon dioxide was calculated by the perfect gas laws; 1 mol is produced per mol of carbodiimide.[5] This technique gave the proper carbodiimide content for dicyclohexylcarbodiimide. By this method the carbodiimide contents of M and P were found to be 2.3×10^{-3} and 3.0×10^{-3} equiv/g, respectively. Multiplying 3×10^{-3} by the molecular weight of P, 600, gives 1.8 equiv/mol, i.e., about 2 groups/molecule.

Infrared spectroscopy using the maximum at 2160–2170 cm^{-1} [6] was used to measure the concentration of M and P after reaction. For calibration, known amounts of M and P were dissolved in solutions of polyester in tetrahydrofuran (1:10, w/v). Spectra of these solutions in 0.15-mm-thick cells were taken by using a carbodiimide-free solution of polyester in tetrahydrofuran in the reference beam of the double-beam instrument. Five- and tenfold expansions of the transmission were used at dilute concentrations of the carbodiimides. The calibration data are in Figure 1, plotted in the form $\ln (I_{2250}/I_{\mathrm{Pk}})$ vs. the equivalents of carbodiimide per gram of ester plus carbodiimide, [M] or [P], i.e., on a solvent-free basis. Here I_{2250} is the transmittance, well off the peak, at 2250 cm^{-1} and I_{Pk} is the transmittance at the peak maximum (2165 cm^{-1} for P and 2175 cm^{-1} for M). Polyester–carbodiimide reaction mixtures and bulk polymers were diluted 10:1 with tetrahydrofuran and run in the cell used for the calibrating solutions. Values of $\ln (I_{2250}/I_{\mathrm{Pk}})$ were calculated and [M] and [P] taken from Figure 1. Samples from reactions carried out in tetrahydrofuran were run without dilution.

Acid content, [A] (equiv/g), was measured by dissolving 1–3 g of reaction mixture or polymer in 75 cm^3 of dimethylformamide and titrating the acid with 0.02 N tetrabutylammonium hydroxide, as described previously.[2]

Ordinarily values of [A], [M], and [P] were precise to (0.1–0.2) $\times 10^{-5}$ equiv/g.

The initial acid contents of PCL 530 and PCL 2000 were about 0.5×10^{-5} equiv/g, a value near the level of precision. To increase each [A], 15-g samples were aged at 85 °C above water for about 2 weeks. These then had [A] of about 40×10^{-5} equiv/g. Blends were made with the parent diols to give [A] of about 7×10^{-5} equiv/g. The value was measured after drying the blend at 85 °C for 2 h under vacuum. PBA 930 had [A] initially equal to 7.5 $\times 10^{-5}$ equiv/g, so it was simply dried before use.

Experiments with M in polyester were performed by placing 10–15 g of polyester in a flask containing a magnetic stirring bar. The flask was brought to the desired temperature in an oil bath and the stirrer started. M was added to give a concentration about

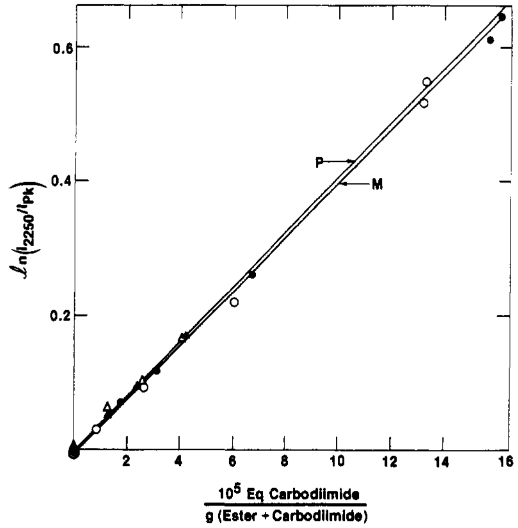

Figure 1. Absorption ratio vs. carbodiimide content: (●) M with PBA 930; (○) M with PCL 2000; (▲) P with PBA 930; (△) P with PCL 2000.

20% larger than [A]. When M had dissolved (about 2 min), the stirrer was stopped. At intervals samples were withdrawn with a heated pipet and values of [A] and [M] measured.

The polymeric carbodiimide was only slightly soluble in the polyesters. Reactions were heterogeneous and attempts to withdraw samples from a flask gave erratic values of [P] because of segregation of the solid. Consequently, runs were done in individual vials each containing 1–2 g of polyester, a 20% excess of P (in one run a 100% excess was used), and a small stirring bar, which rotated at about 100 rpm. At the desired time the contents of each vial were diluted 10:1 with tetrahydrofuran, [P] was measured on a small portion, and [A] was measured by titrating the rest.

Mixtures containing M or P with PBA 930 in tetrahydrofuran were made up by combining equal volumes of stock solutions to give an [A] of about 7 × 10^{-6} equiv/cm^3 with a carbodiimide content about 10–20% higher. Vessels were 50-cm^3 glass ampules fitted with T-shaped glass values having stems of poly(tetrafluoroethylene). The ampules were back-filled with nitrogen after two freeze–evacuate–thaw cycles, which removed some oxygen. The mixtures were homogeneous and so were not stirred during reaction. At intervals the vessels were cooled to room temperature, the valve stems removed, and samples pipetted out for acid and carbodiimide analysis.

A polyester polyurethane was made by forming a 1:2 prepolymer from PBA 930 and bis[4-(isocyanato)phenyl]methane at about 80 °C. 1,4-Butanediol equivalent to the remaining isocyanate was added as a chain extender and the mixture was cured under nitrogen at 70 °C for 5 days. [A] was measured and the polymer was dissolved in enough tetrahydrofuran to make a 10% solution. There was a small amount of gellike material that did not dissolve. This was not separated because of the high viscosity of the solution. About 20% excess carbodiimide was added. The solution was cast onto a sheet of poly(tetrafluoroethylene) in a large desiccator. With P, solvent evaporation was accomplished by passing nitrogen through the desiccator for several days and then applying a vacuum for 2 weeks. With M, the same procedure gave polymer with inconveniently low contents of acid and carbodiimide. Higher values were obtained by applying the vacuum immediately after casting, which cooled the solution, and continuing evacuation for only 2 days.

Each polymer film was nontacky and clear except for bubbles if it contained M but hazy if it contained P. Microscopic examination of the latter film showed a separated phase of spherical particles ranging in diameter from 0.02 mm downward; many were 0.002 mm in diameter. Mechanically, the films behaved as if cross-linked; i.e., they are thermoplastic elastomers.

The films containing P were packed in 4A molecular sieves in glass tubes and placed in thermostated baths. At intervals pieces were removed and analyzed to determine [A] and [P]. The same procedure with film containing M resulted in much greater decreases in [M] than in [A]. We judged that this was due to evaporation of M, which probably was adsorbed on the sieves. Evaporation of M at 85 and 55 °C was proved by heating the film under vacuum with no sieve present and catching M in a cold trap. Sieve was therefore eliminated and samples were run for shorter times in order to increase the relative importance of change due to reaction (presumed second order overall) as opposed to change due to evaporation (presumed first order in [M] and zero order in [A]).

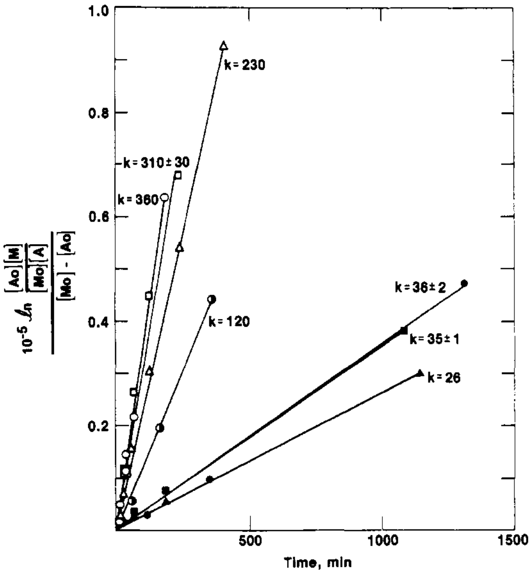

Figure 2. Reaction of polyester acid with monomeric carbodiimide. (○, ◐, ●) PBA 930, $10^5[M_0] = 9.0$, $10^5[A_0] = 7.4$; (△, ▲) PCL 530, $10^5[M_0] = 8.0$, $10^5[A_0] = 6.7$; (□, ■) PCL 2000, $10^5[M_0] = 8.4$, $10^5[A_0] = 7.0$ (unshaded symbols, 85 °C; half-shaded, 70 °C; shaded, 55 °C). Concentrations in equiv/g. *k* are rate constants in g/(equiv·min).

Polyester viscosities were measured with a rotating viscometer. Values ranged from 3.2 Pa·s (1 Pa·s = 10 cP) for PCL 530 at 85 °C to 64 Pa·s for PCL 2000 at 55 °C.

Results

Monomeric Carbodiimide in Polyester. Aromatic carbodiimides and carboxylic acids react to form 1:1 adducts known as acylureas:[6]

$$\text{-CO}_2\text{H} + \text{-N=C=N-} \xrightarrow{k} \text{-CONCONH-}$$

Except for reactions in tetrahydrofuran, our results at greater than 50% acid consumption confirm 1:1 stoichiometry. If the reaction obeys second-order kinetics, then rates as functions of time, *t*, are

$$-\mathrm{d}[M]/\mathrm{d}t = -\mathrm{d}[A]/\mathrm{d}t = k[A][M]$$

For initial concentrations $[M_0] > [A_0]$, integration gives[7]

$$\ln([A_0][M]/[M_0][A])/([M_0] - [A_0]) = kt \qquad (1)$$

Thus values of the quotient should increase proportionally with time with a slope *k* that is the second-order rate constant. Figure 2 is a plot of our data for the monomeric carbodiimide in polyester diols.

Imprecision in [M] and [A] may make $[A_0]/[M_0]$ appear less than [A]/[M] at low extents of reaction, thereby making the logarithm slightly negative. However, if $[A_0]$ is less than $[M_0]$ and the change in [A], Δ[A], is negative and equal to the change in [M], Δ[M], then $[A_0]/[M_0]$ must be greater than [A]/[M]. To avoid negative logarithms the [M] and [A] hereafter, unless otherwise specified, are $[M_0] + (\Delta[A] + \Delta[M])/2$ and $[A_0] + (\Delta[A] + \Delta[M])/2$, respectively.

Values of *k* in g/(equiv·min) are entered in Figure 2 at the largest ordinate value plotted. These *k* values were

Table I
Reaction of Acid of PBA 930 Polyurethane with Monomeric Carbodiimide[a]

temp, °C	time, min	10^5[A], equiv/g	10^5[M], equiv/g	k, g/(equiv·min)
23	1440	1.8	2.6	6
23	11520		1.3	6[b]
35	4030	1.1	1.7	10
55	1020	0.9	1.3	55
85	245	0.9	1.4	210

[a] $[A_0] = 2.4 \times 10^{-5}$ equiv/g; $[M_0] = 3.0 \times 10^{-5}$ equiv/g.
[b] Assumed $\Delta[A] = \Delta[M] = 1.7 \times 10^{-5}$ equiv/g.

calculated by least-squares analysis forcing the lines through the origin. Standard errors here and in other data are less than one in the last nonzero digit, except as indicated. These units of k are convenient for polyesters and polymers which are solids at room temperature. Division by the density, 1.01–1.07 g/cm^3, gives k in cm^3/(equiv·min) if volume units are desired.

Reactions run to the final times shown in Figure 2 consumed 75–93% of $[A_0]$. Thus second-order kinetics describes the data adequately over most of the possible range.

The samples PCL 2000 and PBA 930 crystallize at temperatures below 55 °C, so experiments with polyesters were only run in solution at lower temperatures.

Monomeric Carbodiimide in Polyurethane. PBA 930 had an initial acid content of about 7.5×10^{-5} equiv/g. Reaction of PBA with diisocyanate and butanediol to form a 1:2:1 polyurethane diluted the acid, theoretically to 4.8×10^{-5} equiv/g. The value actually measured was 4.7×10^{-5} equiv/g, demonstrating conservation of acidity during urethane formation. Addition of 20% excess M, a concentration of 5.5×10^{-5} equiv/g, should dilute the acidity to 4.5×10^{-5} equiv/g because of the added mass. After the slow solvent evaporation described in the Experimental Section, values of 10^5[A] and 10^5[M] were 1.1 and 1.8 equiv/g, respectively. The more rapid solvent evaporation gave values of 2.4 and 3.0 for 10^5[A] and 10^5[M], respectively. Obviously there is a time-dependent reaction between carbodiimide and acid during evaporation.

The film with these last values of [A] and [M] gave the data in Table I. The rubbery character permitted measurable reaction even at 23 °C. Only one result at each temperature was taken because only about 10 g of film was available. Thus the rate constants in Table I are calculated from single aging times, by assuming second-order kinetics, and no standard error can be calculated. The values of k are about the same as those in the polyesters.

Polymeric Carbodiimide in Polyesters. Considerable complexity was anticipated in working with P. To the eye it appeared incompletely soluble even at 0.1% by weight (about 0.3×10^{-5} equiv/g), but this observation would not necessarily preclude solution of some low molecular weight components. The observed softening suggests that the glass temperature is somewhat lower than 65 °C. If P sorbed much polyester, one would expect it to be soft at 55 °C, but the particles of P did not stick together when immersed in polyesters for 3 weeks. At 85 °C, P particles agglomerated into larger sticky globules in about 1 day. Thus the range 85–55 °C probably includes the glass temperature of P. Particles of P also tended to settle out despite the stirring. This was most marked with PCL 2000 at 55 °C, presumably because it is the most viscous medium.

Despite the foregoing complications, the kinetics appear to be second order as shown in Figure 3. Experiments in PCL 530 with initial [P] that differed by a factor of 2 gave the same values of k, consistent with second-order kinetics. This would be expected if the rate is proportional to surface area and the stirring maintains the initial surface-to-volume ratio in the P particles.

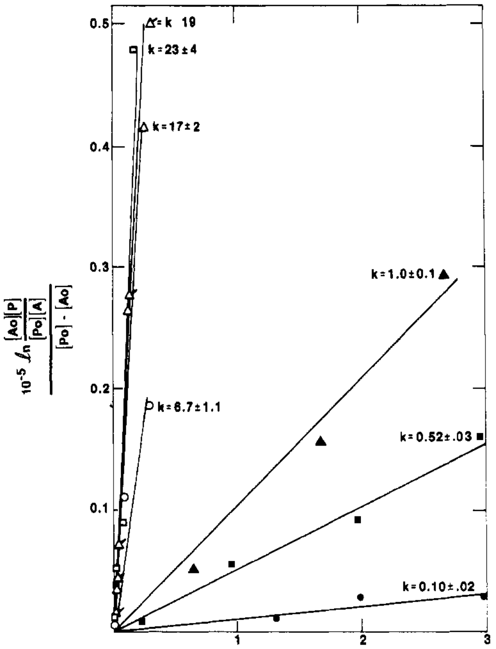

Figure 3. Reaction of polyester acid with polycarbodiimide. $10^{-5} \ln([A_0][P]/[P_0][A])/([P_0] - [A_0])$ vs. time: (○, ●) PBA 930, $10^5[P_0] = 9.2$, $10^5[A_0] = 7.6$; (△) PCL 530, $10^5[P_0] = 7.8$, $10^5[A_0] = 6.6$; (Δ̸) PCL 530, $10^5[P_0] = 12.5$, $10^5[A_0] = 6.3$; (▲) PCL 530, $10^5[P_0] = 5.9$, $10^5[A_0] = 3.2$; (□, ■) PCL 2000, $10^5[P_0] = 7.5$, $10^5[A_0] = 6.2$ (shaded, 55 °C; unshaded, 85 °C). Concentrations in equiv/g. k are rate constants in g/(equiv·min).

Values of k at 85 °C are 10-fold less than with M. At 55 °C quite different k are obtained from the different polyesters, values being 30- to 300-fold less than for M at 55 °C. The glass temperature of P, polyester viscosity (which affects stirring rate), and differences in polyester–carbodiimide compatibility can all affect the rate constant and we have no clear explanation of the observed differences in k.

Polycarbodiimide in Polyurethane. Measured initial values of [A] and [P] in the polyurethane were 3.2 and 4.4×10^{-5} equiv/g, respectively. If no reaction had occurred during solvent evaporation, values would have been 4.6 and 5.5×10^{-5} equiv/g. Thus reaction during evaporation was not as much a problem as with M.

Figure 4 shows the behavior of the apparent second-order rate constant. At times under 3900 min at 85 °C only [P] was measured in order to conserve the polymer. For calculations at such times the observed Δ[P] was assumed to equal Δ[A]. At each temperature the ordinate rises less rapidly as time increases, becoming nearly constant at 55 and 35 °C. Thus the rate becomes slower than predicted by second-order kinetics. Later this behavior will be attributed to limited mobility of the reactants. Initially, ease of approach may be less restricted, and we will assume that true rate constants are given by the initial slopes, which are denoted k_0 and entered on Figure 4. These values are subjective estimates since the data show curvature at all times and the proper functional form is not known. The k_0 are greater than k for polycarbodiimide in PBA 930. The plateau is higher at 55 °C than at 35 °C, suggesting that the readily consumable portion of reactants increases with temperature. These portions amount to about 20%

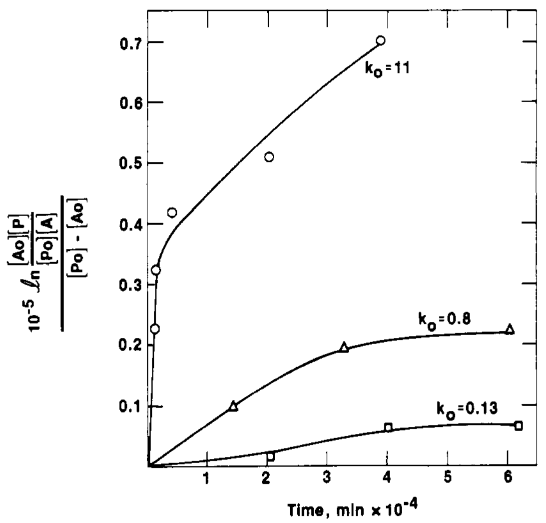

Figure 4. Reaction of polyester acid in PBA polyurethane with polycarbodiimide. 10^{-5} ln $([A_0][P]/[P_0][A])/([P_0] - [A_0])$ vs. time: (○) 85 °C; (△) 55 °C; (□) 35 °C. $10^5[P_0] = 4.4$, $10^5[A_0] = 3.2$ equiv/g. k_0 are initial slopes in g/(equiv·min).

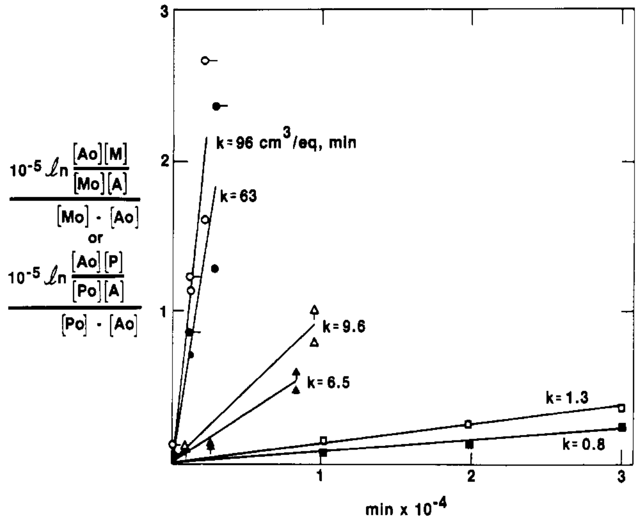

Figure 5. Reaction of PBA 930 acid and carbodiimide in tetrahydrofuran. 10^{-5} ln $([A_0][M]/[M_0][A])/([M_0] - [A_0])$ or 10^{-5} ln $([A_0][P]/[P_0][A])/([P_0] - [A_0])$ vs. time: (○, ●) 85 °C; (△, ▲) 55 °C; (□, ■) 35 °C (shaded: P, $10^5[P_0] = 0.94$, $10^5[A_0] = 0.67$ equiv/g; unshaded: M, $10^5[M_0] = 0.77$, $10^5[A_0] = 0.68$ equiv/g). For symbols with bars it was assumed that the observed $\Delta[M]$ or $\Delta[P]$ equals $\Delta[A]$. k are slopes intermediate between those for barred and unbarred points.

and 50% of the acid at 35 and 55 °C, respectively, and somewhat smaller percentages of polycarbodiimide. At 85 °C more than 80% of the acid was consumed with no plateau evident.

Reaction of Carbodiimides and Polyester Acid in Tetrahydrofuran. The rather narrow range of *k* in polyesters and the elastomer made us curious to measure the rate constants in a solution of ordinary viscosity. Tetrahydrofuran was used because it dissolves M, P, and the polyesters. A complication was that at the longer times at 85 and 55 °C, $\Delta[A]$ (now in equiv/cm³) was always less than $\Delta[M]$ or $\Delta[P]$. Blanks were run with M and P in polyester-free tetrahydrofuran and with PBA 930 in carbodiimide-free tetrahydrofuran. Carbodiimide did not disappear from the polyester-free blanks nor did significant acidity develop with or without carbodiimide. Thus we have no explanation for the observation.

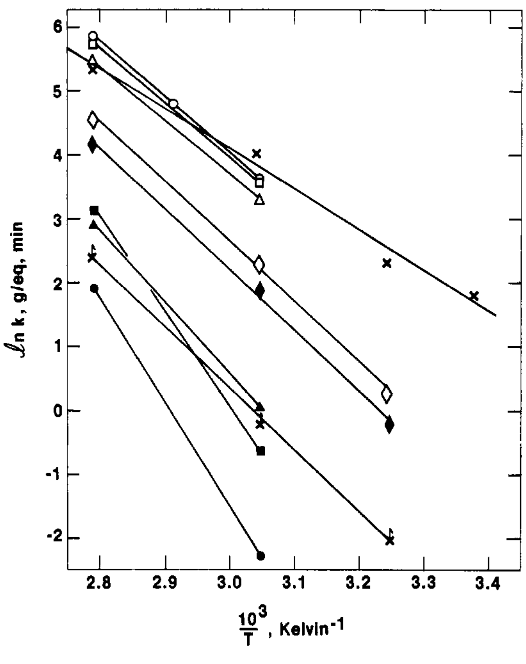

Figure 6. Arrhenius plot for reactions of polyester acid with carbodiimides. Polyester diols: (○, ●) PBA 930; (△, ▲) PCL 530; (□, ■) PCL 2000; (◇, ◆) PBA 930 in tetrahydrofuran. Polyurethane: ×, ӿ. Monocarbodiimide: unshaded symbols, ×. Polycarbodiimide: shaded symbols, ӿ.

Table II
Activation Energies and Preexponential Terms for Reaction of Polyester Acid and Carbodiimide

reaction	act energy, kJ/mol[a]	preexponential, cm³/(molecule·s)
M + polyester[b]	75	6×10^{-13}
M + polyurethane	53 ± 5	2.5×10^{-16}
M + PBA 930 in THF	79 ± 3	7.8×10^{-13}
P + PCL 2000	95	6.6×10^{-7}
P + PCL 530	124	2.5×10^{-11}
P + PBA 930	138	1.7×10^{-5}
P + polyurethane	82 ± 3	2.3×10^{-13}
P + PBA 930 in THF	80 ± 4	7.7×10^{-13}

[a] 1 kJ equals 0.239 kcal. [b] Average of values for three polyester diols.

Data were calculated for the second-order plot in two ways. One used the average change in [A] and [M] or [P] as before. The other way took the change in [A] as being equal to the observed change in [M] or [P]. All sets of results are plotted in Figure 5. Those from the first calculation curve downward while those from second curve upward, suggesting that acid formed but consumed carbodiimide to some extent. We take *k* as being between the two sets of points. This is not at all rigorous but it will permit comparison with values in polyester and elastomer.

Values of *k* for P are about 30% less than those for M. Both sets of *k* are between those for M and P in the diols.

Arrhenius Plot. Figure 6 is an Arrhenius plot of all the *k*. Table II contains activation energies and preexponential factors, the latter calculated in cm³/(molecule·s) units. The preexponentials in the homogeneous reactions, i.e., those involving M and also that with P in tetrahydrofuran, are well below the collision frequency, about 2×10^{-10} cm³/(molecule·s), indicating that there is a significant entropic term. Preexponentials for the heterogeneous reaction of P in the polyesters are very large but their significance is unknown. Rate constants for reaction of M and P in polyurethane have lower activation energies and preexponentials than do corresponding rate constants in the polyesters. The urethane group is too remote from the acid group to have an inductive or mesomeric effect.

Perhaps there is association between carbodiimide and urethane that affects the activation energy.

Discussion

The wet-aging process used to bring the PCL polyesters to the desired acid content affects the molecular weight. Consider PCL 2000, for which the percentage change is the greatest. Introduction of 40×10^{-5} equiv of acid/g means that the same number of scissions have occurred, since each acid group results from hydrolysis of an ester linkage. This reduces the molecular weight from 2000 to about 1100. The wet-aged material is then blended with the original to give [A] of 7.5×10^{-5}; the molecular weight of the blend will be about 1800. In the blend about one molecule in seven has an acid end. With PCL 530 the percentage change in molecular weight is much less, as is the percentage of molecules with an acid end. It is unlikely that these molecular weight changes affect the k since no consistent differences were found between k for the three polyesters.

Except for P in polyurethane the data fit eq 1 quite well. The range of k is relatively small, particularly where monocarbodiimide is concerned. This can be made to appear plausible by the argument below.

If reaction is not diffusion controlled $k \ll 4\pi\rho D$, where ρ is the separation of centers at the time of reaction and D is the mutual diffusion coefficient of A and M.[8] ρ cannot be less than 10^{-8} cm. We estimate a value for D by taking a value, 5×10^{-5} cm^2/s, typical of small molecules in solvents of about 5×10^{-2} Pa·s viscosity[8] and scaling it inversely to bulk viscosity. On the rubbery plateau the shear viscosity is about 2×10^5 Pa·s.[9] Thus D in the rubber might be 10^{-13} cm^2/s, so $4\pi\rho D$ is about 10^{-20} cm^3/(molecule·s). The largest value of k in the rubber is 210 g/(equiv·min) or 0.6×10^{-23} cm^3/(molecule·s). Therefore, lack of diffusion control is plausible.

In the polyurethane made from PBA 930 about one soft (polyester) segment in 14 will have an acid end. On average, for each soft segment there is a hard segment consisting of residues from a butanediol molecule and a bis[4-(isocyanato)phenyl]methane molecule between two urethane groups. The hard segments are pictured as associating in some fashion to give effective cross-links. Therefore, each acid group in a sense is tethered to the effective cross-link so that its range of motion is restricted. There are about 50 C–C or CO bonds per chain in PBA 930, making the radius of the accessible volume about 5×10^{-7} cm. The amount of P is about equal to the acid content. Microscopic examination shows that P segregates into spheres, whose average diameter appears to be about 2×10^{-4} cm. Thus it appears that if the spheres and the cross-links are fixed in place, some acid will not be able to reach carbodiimide molecules, explaining the plateaus in Figure 4. As temperature increases, the moduli of thermoplastic polyurethane elastomers eventually decrease, as evidenced by the fact that they are moldable, suggesting that the hard-segment association weakens. If a hard segment to which an acid-ended soft segment is attached becomes mobile, then the effective length of the tether is increased and so more carbodiimide becomes accessible. The glass temperature of the polycarbodiimide must also be a factor, since above it all molecules in the spheres should become accessible. In this manner one can rationalize the increase in plateau level with temperature and the apparent lack of a plateau at 85 °C. The content of species close enough together to be considered unrestricted is highest initially; hence, our use of the initial slope as the second-order rate constant of P in polyurethane.

A manuscript is in preparation that describes the hydrolysis of polyester polyurethanes in the presence of M and P. These appear about equally effective at the level used, (5–9) $\times 10^{-5}$ equiv/g polymer. At 100% relative humidity at 85 and 55 °C the added service life amounts to about 20 and 330 days, respectively.

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