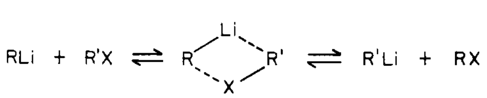
Macromolecules 1982, *15*, 453-458

3. Formation of Exchange Products. Lithium-halogen exchange reactions are generally explained by two types of mechanisms: (i) an ionic four-center mechanism:[10]



and (ii) a radical mechanism according to

$$\mathrm{RLi} + \mathrm{R'X} \rightleftharpoons [\mathrm{R\cdot,X,Li,R'\cdot}] \rightleftharpoons \mathrm{R'Li} + \mathrm{RX}^{11}$$

It is known that these reactions are equilibria and that the formation of the more stable carbanion is favored.[12]

(a) A reaction such (A), exchange between an alkyl iodide and an alkyllithium, will lead to comparable amounts of the two organolithiums, as demonstrated by the study of the exchange of *n*-butyllithium ethyl iodide.[13] Thus this reaction is likely to occur but its importance cannot be evaluated.

(b) Reactions C_1 and E_1 involve an exchange between the dienyllithium and an alkyl halide. These reactions are expected to favor the formation of the stabilized species R–M–Li. But our results indicate that R–M_2–R is formed in a process that modifies the distribution of the oligomerization numbers, and among the different possibilities, it can only be the route $C_1/E_1,G_1$.

The coupling reaction was reported in two cases to proceed by an S_n2 mechanism: (i) between an allylic halide and an organolithium[14] and (ii) between an allylic organolithium and an alkyl halide.[15] In the view of this mechanism, one may expect the high reactivity of the allylic halide R–M–X in reaction G_1 to displace toward the right the equilibria C_1 and/or E_1.

Finally, one may try to explain why DB gives a higher yield of the exchange product R–M_2–R than the two other dienes: if as suggested in section 2 (dimethylbutadienyl)lithium is less stabilized by delocalization, reactions C_1 and E_1 will be less disfavored than for the two other dienyllithiums.

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Hydrolytic Degradation of Polyester Polyurethanes Containing Carbodiimides

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ABSTRACT: Polyester polyurethanes containing a mono- or polycarbodiimide were aged at 100% relative humidity at 85, 55, and 35 °C. Acid concentration, [A], carbodiimide concentration, [B], and the number-average molecular weight, M_n, were measured at intervals. Results are consistent with the occurrence of three parallel processes: acid-catalyzed hydrolysis, reaction of acid with carbodiimide, and uncatalyzed hydrolysis. Their rate constants are designated k (pseudo first order), k' (second order), and k_0 (pseudo zero order), respectively. Pertinent differential equations are $d[A]/dt = k_0 + k[A] - k'[A][B]$, $d\Delta(M_n^{-1})/dt = k_0 + k[A]$, and $-(d[B]/dt) = k'[A][B]$. The constants k, k', and k_0 were calculated from the rates of scission and acid formation without carbodiimide, of mutual disappearance of A and B without water, and of long-term disappearance of B in the presence of water, respectively. These constants and the initial values of [A], [B], and M_n were inserted into the differential equations above and the equations were integrated digitally. The curves generated describe hydrolysis in the presence of monocarbodiimide reasonably well. Lifetimes, defined as the time required to accumulate a specific number of scissions, are increased 3-fold at 85 °C, 7-fold at 55 °C, and about 10-fold at 35 °C by use of about 3 wt % monocarbodiimide. The polycarbodiimide is insoluble in the polyurethanes, and curves generated as described above do not fit the hydrolysis very well. By observation at 85 °C the polycarbodiimide is about as effective as the monocarbodiimide. The rate constant k_0 is critical to the lifetime increment. It equals about 10^{-6} equiv/(g·day) at 85 °C and has an activation energy of about 85 kJ/mol.

Introduction

The hydrolytic degradation of unstabilized polyester polyurethanes is due to the acid-catalyzed hydrolysis of the ester linkage.[1] Acid concentration, [A], and the reciprocal of the number-average molecular weight, M_n^{-1}, change by equivalent amounts, obeying the equations[2]

$$d[A]/dt = d\Delta(M_n^{-1})/dt = k[A] \qquad (1)$$

Here t is time and k is a pseudo-first-order rate constant giving the fractional rate of increase in acid content.

Certain mono- and polycarbodiimides stabilize polyester polyurethanes against hydrolysis by reacting with acid to form acylureas.[3] The kinetics of this reaction have been studied in dry polyester diols and in a dry polyester polyurethane.[4] With a soluble monocarbodiimide, M, acid and carbodiimide contents obey the equations

$$-d[A]/dt = -d[M]/dt = k'[A][M] \qquad (2)$$

More complex behavior, described later, was found with

Table I
Polymer Characteristics before Aging

material	$10^5[A_0]$, equiv/g	$10^4(M_n)_0$	$10^5[M_0]$ or $10^5[P_0]$, equiv/g
63PBA0	1.2	1.8	0
63PBA8.9M[a]	0.5	1.6	5.3
63PBA8.9M[b]	0.5	2.1	5.3
73PBA0	1.0	2.7	0
73PBA4.9M	0.2	1.6	2.6
73PBA6.9P	0.2	1.9	5.3
66PCL0	0.5	2.4	0
66PCL4.6M	0.4	2.1	3.6
66PCL6.0P	0.7	1.7	4.3

[a] Precipitated from THF with water. [b] Cast from THF.

a polycarbodiimide, P, which was insoluble in the polyester polyurethane.[4]

For this paper, hydrolytic degradation of polyurethanes in the presence of carbodiimides was studied at 85, 55, and 35 °C.

Experimental Section

The carbodiimides were the same as used previously.[4] M was a commercial grade of bis(2,6-diisopropylphenyl)carbodiimide containing 2.3×10^{-3} equiv of carbodiimide/g. The exact structure of P was not established. Infrared spectra indicated that it contained aliphatic groups and a highly substituted aromatic ring. The carbodiimide content was 3.0×10^{-3} equiv/g and M_n, estimated by gel permeation chromatography (GPC), was about 600, giving about 2 carbodiimide groups per molecule.

Poly(butylene adipate) (PBA) and polycaprolactone (PCL) diols had M_n equal to 1600 and 1230 and [A] equal to 2.1×10^{-5} and 0.4×10^{-5} equiv/g, respectively. Polyurethanes of 1:2:1 mole ratio were prepared from either poly(ester diol), 4,4′-diphenylmethane diisocyanate (registry no. 101-68-8) (MDI), and 1,4-butanediol by first making a polyester–diisocyanate prepolymer, to which butanediol was added. The final cure was at 70 °C under dry nitrogen for about 1 week. No catalyst was used for the urethane-forming reactions. If the presence of a carbodiimide was desired, it was mixed with the poly(ester diol) and heated at 85 °C for 2 h before the prepolymer was made. Monocarbodiimide was also incorporated in a commercial polymer of MDI, PBA (63 wt %), and 1,4-butanediol by dissolving M in a solution of this polymer in tetrahydrofuran. The solvent was removed, either by evaporation under vacuum to form a 0.2-mm-thick sheet or by pouring the solution into water and subjecting the precipitate to a vacuum. This last and the other bulk polymers were molded at about 180 °C into 0.5-mm-thick sheets, which were cut to form strips 9 mm wide. These were aged above distilled water in sealed glass tubes immersed in regulated oil or water baths.

Before and after the polymers were aged, M_n, [A], and [M] or [P] were measured by GPC, titration, and infrared analysis, respectively.[2,4] Values of M_n were precise to about 10% and values of [A] and [M] or [P] were precise to about 10^{-6} equiv/g. An acid analysis was not done after every time interval because it required much more sample than the other two analyses. Some tensile strengths were measured and correlated with changes in M_n^{-1}. It was established that the occurrence of 10^{-4} (mol of scissions)/g resulted in almost complete loss of strength for all polymers.

Initial characteristics of the polymers are in Table I. The first two numbers of the material code give the weight percent of polyester on a carbodiimide-free basis. Letters that follow identify the polyester. The second number is the amount of carbodiimide charged in 10^5 equiv/(g of polymer). This amounted to 3–5 wt % of the polyester. A final letter identifies the carbodiimide if one was used. The measured carbodiimide contents before aging (last column) are always less than the amount charged, probably because of reaction with acid and evaporation during molding.[4]

Results

Preliminary Considerations. Data will be interpreted in terms of three reactions:

$$H_2O + -CO_2- \xrightarrow{k_0} -CO_2H(A) + HO- \quad (3)$$

$$H_2O + -CO_2- \xrightarrow[A]{k} A + HO- \quad (4)$$

$$A + B \xrightarrow{k'} \text{acylurea} \quad (5)$$

Here (3) is the uncatalyzed hydrolysis of ester to form carboxylic acid tipped polyester (A) and hydroxyl tipped polyester. Reaction 4 represents the acid-catalyzed hydrolysis and reaction 5 is the mutual reaction of A with either P or M, both represented by B. For small extents of degradation the ester and water contents change little with aging. Hence k_0 is effectively a zero-order rate constant, k a first-order rate constant, and k' a second-order rate constant. Units used are based on 1 g of polymer, i.e., equiv./(g·day) for k_0, day^{-1} for k, g/(equiv·day) for k', and (mol of scissions)/g for $\Delta(M_n^{-1})$. The differential equations for the variation with time of [A], $\Delta(M_n^{-1})$, and [B] are

$$d[A]/dt = k_0 + k[A] - k'[A][B] \quad (6)$$

$$d\Delta(M_n^{-1})/dt = k_0 + k[A] \quad (7)$$

$$-d([B])/dt = k'[A][B] \quad (8)$$

Equations 6 and 7 reduce to eq 1 if [B] equals zero and k_0 is small compared with k[A]. Strictly, eq 7 is valid only with M, since the polyfunctionality of P tends to increase M_n. Alternative mechanisms considered and rejected are discussed later.

Values of k come from aging studies without carbodiimide. For example, that for 63PBA0 at 85 °C is 0.2 day^{-1};[2] the other polymers give similar values shown below. In ref 4, k' at 85 °C with M was found to be 3×10^5 g/(equiv·day) in a dry PBA polyurethane. This value will be used for all polymers containing M. The value of k_0 is estimated as follows. With monocarbodiimide, $k'[B_0]$ is in the range 7–15, much greater than k, so [A] initially decreases rapidly according to eq 6 and quickly reaches a pseudo-steady-state concentration in which $k_0 \gg k[A]$. Then eq 6 and 7 respectively reduce to

$$d[A]/dt \approx k_0 - k'[A][B] \approx 0 \quad (6')$$

$$d\Delta(M_n^{-1})/dt \approx k_0 \quad (7')$$

From (6′), the steady-state concentration of A is approximately equal to $k_0/k'B$, which on substitution in (8) gives

$$-d[B]/dt \approx k_0 \quad (8')$$

Thus after a short aging period the rates of scission and disappearance of B should become constants, equal to one another and to k_0. Calculations will generally be based on the disappearance of B since an imprecision of 10% in M_n makes $\Delta(M_n^{-1})$ imprecise by about 10^{-5} (mol of scissions)/g, frequently a large fraction of the measured value.

Stabilization with Monocarbodiimide. Figure 1 is a plot of [A], $\Delta(M_n^{-1})$, and [M] for 73PBA0 and 73PBA4.9M vs. aging time at 85 °C. Data for 73PBA0 should follow exponential functions obtained by integrating eq 1; i.e., $[A] = [A_0]e^{kt}$ and $\Delta(M_n^{-1}) = [A_0](e^{kt} - 1)$, $[A_0]$ being the initial value of [A]. The solid and dashed lines on the left were calculated by these functions with $k = 0.26$ day^{-1}. For 76PBA4.9M values of $\Delta(M_n^{-1})$ rise by about 1.8×10^{-5} mol/g in 16 days, giving a slope equal to 1.1×10^{-6} (mol of scissions)/(g·day). Values of [M] fall by about 2×10^{-5} equiv/g in 16 days, giving a slope equal to -1.3×10^{-6} equiv/(g·day). Thus $d\Delta(M_n^{-1})/dt$ is approximately equal to $-d[M]/dt$ as suggested above and k_0 will be taken as 1.2×10^{-6} equiv/(g·day). In the unstabilized polymer,

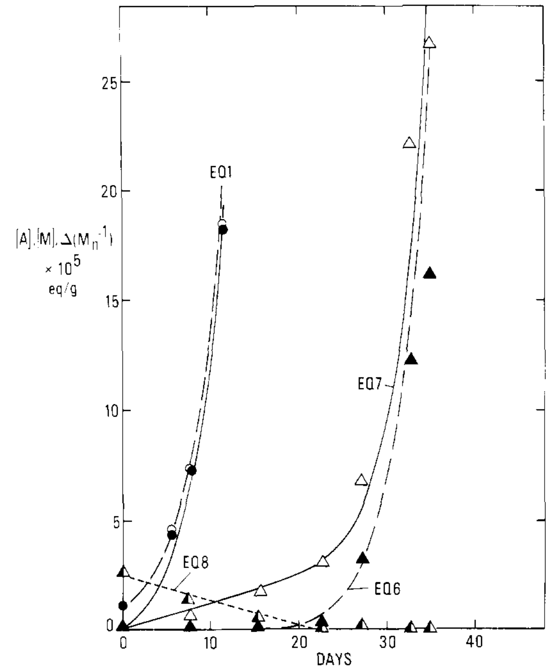

Figure 1. Hydrolytic degradation of 73PBA0 (circles) and 73PBA4.9M (triangles) at 85 °C. Lines by integration of indicated equations with $k_0 = 1.2 \times 10^{-6}$ equiv/(g·day), $k = 0.26$ day^{-1}, and $k' = 3 \times 10^5$ g/(equiv·day). (△, ○, —) $\Delta(M_n^{-1})$; (▲, ●, – – –) [A]; (▲, - - -) [M].

$k[A_0]$ is about 2.6×10^{-6} equiv/(g·day), about twice k_0; as [A] increases, k_0 becomes relatively less important. Thus, without B, eq 6 approximates eq 1.

The set of equations defined by 6–8 is not readily integrable to give solutions in closed form. Consequently, integration was performed on a digital computer using a program provided for ordinary differential equations based on extrapolation of rational functions.[5] The line of short dashes and the solid and dashed lines on the right result from these calculations. A detail not apparent because of the scale of the plot is that A decreases by a factor of 10 in the first half day and then increases slowly as M decreases, getting back to A_0 in about 18 days. Afterward, $[M] \approx 0$ so [A] and $\Delta(M_n^{-1})$ vary approximately exponentially with time. Thus the integration can be checked at long times. It can also be checked at very short times, less than 0.2 day, since then eq 2 should be approximately valid. At both ends of the time scale the computer integration gives results within a few percent of values calculated by these approximating functions.

It is observed with this and the other polymers that measured values of [A] in its range of slow variation are consistently about 10^{-6} equiv/g whereas predicted values are 10^{-7} equiv/g. Also, M usually remains detectable for longer periods than calculation predicts. Probably there are small systematic errors in the analytical methods that account for these observations.

The stabilization resulting from the presence of M is the horizontal displacement between the $\Delta(M_n^{-1})$ lines for 73PBA0 and 73PBA4.9M, about 20 days if failure is represented by the accumulation of 10^{-4} (mol of scissions)/g.

Figure 2 shows similar results, also at 85 °C; for 66PCL0 and 66PCl4.6M. k is 0.19 day^{-1}. Values of $\Delta(M_n^{-1})$ scatter, so k_0 was calculated to be 1.1×10^{-6} equiv/(g·day) from the disappearance of M between 1 and 19 days. The initial rapid decrease in [M] is easily discernible in this theoretical calculation because of the larger value of $[A_0]$; that is, [M] decreases rapidly until it is about equal to $([M_0] - [A_0])$. The agreement between observation and calculation is not as good as in Figure 1. At the level used, M would impart about 25 additional service days at 85 °C.

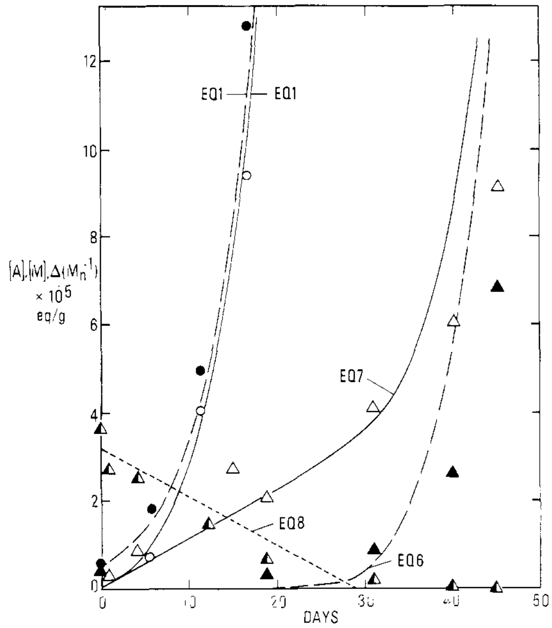

Figure 2. Hydrolytic degradation of 66PCL0 (circles) and 66PCL4.6M (triangles) at 85 °C. Lines by integration of indicated equations with $k_0 = 1.1 \times 10^{-6}$ equiv/(g·day), $k = 0.19$ day^{-1}, and $k' = 3 \times 10^5$ g/(equiv·day). (△, ○, —) $\Delta(M_n^{-1})$; (▲, ●, – – –) [A]; (▲, - - -) [M].

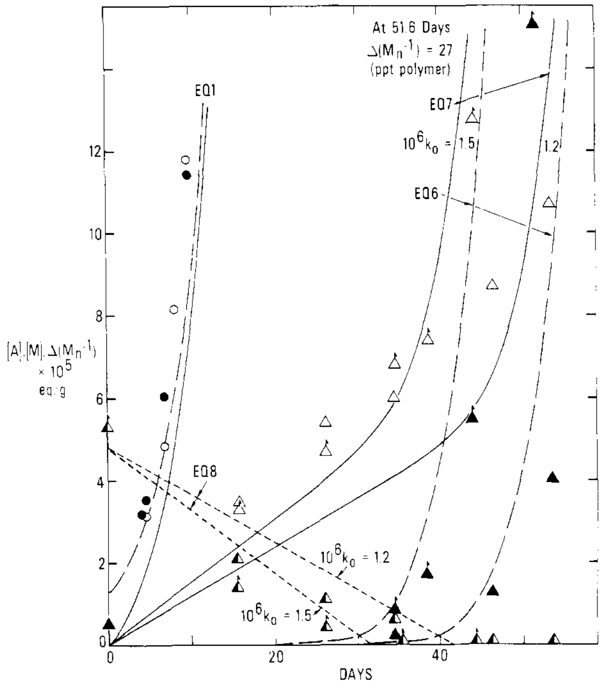

Figure 3. Hydrolytic degradation of 63PBA0 (circles) and 63PBA8.9M (triangles) at 85 °C. Lines by integration of indicated equations, with k_0 as indicated in equiv/(g·day), $k = 0.2$ day^{-1}, and $k' = 3 \times 10^5$ g/(equiv·day). (△, ○, —) $\Delta(M_n^{-1})$; (▲, ●, – – –) [A]; (▲, - - -) [M]. No flag, cast from tetrahydrofuran; flags, precipitated from tetrahydrofuran with water.

Figure 3 gives data obtained with the commercial polymers 63PBA0 and 63PBA8.9M at 85 °C. The value $k = 0.2$ day^{-1} and the data for 63PBA0 come from earlier work[2] in which most of the [A] and $\Delta(M_n^{-1})$ were larger than convenient to plot here. The values that fit in Figure 3 happen to fall above the corresponding exponential curves. k_0 was calculated to be 1.5×10^{-6} equiv/(g·day) from $[M_0] - [A_0] - (0.8 \times 10^{-5})]/26$, where $([M_0] - [A_0])$

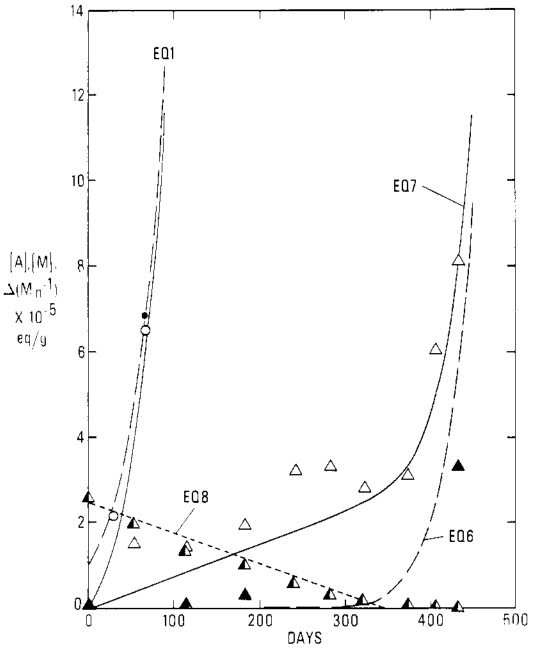

Figure 4. Hydrolytic degradation of 73PBA0 (circles) and 73PBA4.9M (triangles) at 55 °C. Lines by integration of indicated equations with $k_0 = 0.72 \times 10^{-7}$ eq/(g·day), $k = 0.028$ day^{-1}, and $k' = 0.8 \times 10^5$ g/(equiv·day). (△, ○, —) $\Delta(M_n^{-1})$; (▲, ●, – – –) [A]; (◭, - - -) [M].

represents [M] after the initial decrease in [M] and 0.8 × 10^{-5} equiv/g is the value of [M] after 26 days (mean of values for cast and precipitated polymers). Calculations were also performed with $k_0 = 1.2 \times 10^{-6}$ equiv/(g·day) in order to demonstrate how strongly its value affects the service life prediction. Experimentally, about 30 days of additional life was found. We have no explanation for the systematic differences found for cast and precipitated polymers.

Figure 4 gives results for 73PBA0 and 73PBA4.9M at 55 °C. k is 0.028 day^{-1} and k', taken from ref 4, is 0.8 × 10^5 g/(equiv·day). k_0 is calculated to be 0.72 × 10^{-7} equiv/(g·day) from [M] equal to 2.0 × 10^{-5} and 0.3 × 10^{-5} at 50 and 285 days, respectively. The stabilization predicted is about 350 additional days of service. The ratio of lifetime with stabilizer to that without stabilizer is greater at 55 °C than at 85 °C because k_0 decreases more with temperature than k.

Figure 5 gives results for 66PCO0 and 66PC14.6M obtained at 55 °C. k is 0.020 day^{-1} and k' is 0.8 × 10^{-5} g/(equiv·day) at above. k_0 is calculated to be 0.68 × 10^{-7} equiv/(g·day) from [M] equal to 3.1 × 10^{-5} and 0.4 × 10^{-5} equiv/g at 65 and 460 days, respectively.

At 35 °C degradation is very slow even without M. The data obtained to date are listed in Table II. The three negative values for $\Delta(M_n^{-1})$ are not thought to be significant because of the imprecision in values of M_n^{-1}. k was calculated from $[\ln([A_0]/[A_{460}])]/460$ to be 6.2 × 10^{-3} day^{-1} for 73PBA0 and 66PCL0. k' from ref 4 is 0.14 × 10^5 g/(equiv·day). k_0 was calculated to be 1.6 × 10^{-8} and 0.6 × 10^{-8} equiv/(g·day) for 73PBA4.9M and 66PC14.6M, respectively, from $([M_0] - [A_0] - [M_t])/t$, where t is the final time. These values are not significantly different, so their arithmetic mean will be used for both polymers. Integration of eq 1 and 6–8 indicates that 10^{-4} (mol of scissions)/g accumulate at 1.0 and 1.3 years in 73PBA0 and 66PCL0, respectively, and at 7.2 and 9.1 years in 73PBA4.9M and 66PCL4.6M, respectively.

Stabilization with Polycarbodiimide. The mutual disappearance of acid and polycarbodiimide in dry polyester polyurethane did not proceed by simple second-order kinetics.[4] Instead, the apparent second-order rate constant decreased with time, becoming nearly zero at 35 and 55 °C and 10-fold less than the initial value at 85 °C. These changes were attributed to phase separation of the polycarbodiimide, which appeared to be present in spheres approximately 2 μm in diameter. It was argued that the hard-segment blocks, to which the acid groups are connected by polyester chains, restrict the range of motion of acid groups so that some are unable to contact carbodiimide. This work differs in that hydrolytic scission

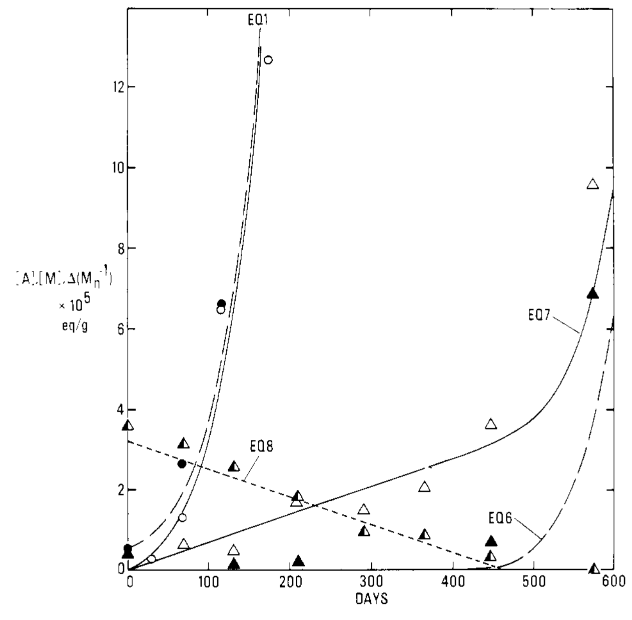

Figure 5. Hydrolytic degradation of 66PCL0 (circles) and 66PCL4.6M (triangles) at 55 °C. Lines by integration of indicated equations with $k_0 = 0.68 \times 10^{-7}$ equiv/(g·day), $k = 0.020$ day^{-1}, and $k' = 0.8 \times 10^5$ g/(equiv·day). (△, ○, —) $\Delta(M_n^{-1})$; (▲, ●, – – –) [A]; (◭, - - -) [M].

Table II
Degradation at 35 °C, 100% Relative Humidity, with and without Monocarbodiimide

time, days	10^5[A], equiv/g	10^5[M], equiv/g	$10^5\Delta(M_n^{-1})$, (mol of scissions)/g
	Polymer 73PBA0		
0	1.0	0	0
112	1.8	0	1.2
266		0	3.9
401	12.3	0	13.9
460	17.7	0	17.6
	Polymer 73PBA4.9M		
0	0.2	2.6	0
119	0.2	1.9	0
290		2.3	0.3
427		1.9	1.4
486		1.6	2.3
	Polymer 66PCL0		
0	0.5	0	0
112	1.1	0	-0.1
307		0	2.1
401	6.5	0	3.9
460	8.6	0	6.0
	Polymer 66PCL4.6M		
0	0.4	3.6	0
129	0.3	3.2	-0.8
309		3.0	-0.3
403	0.2	3.0	0.1
462		2.9	0

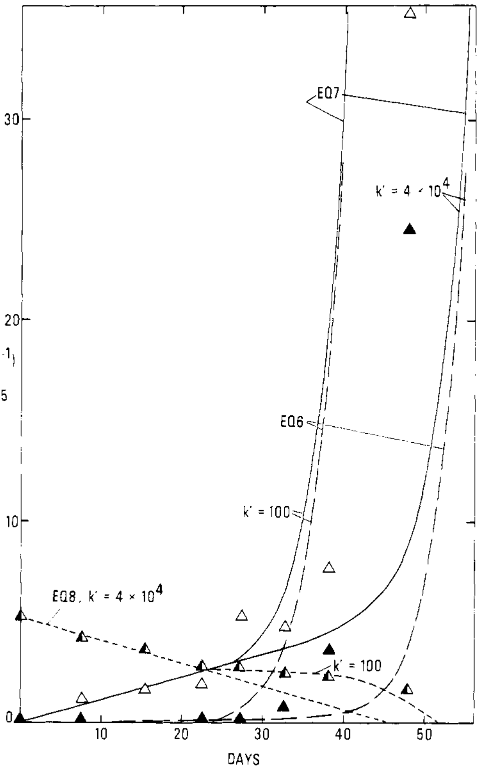

Figure 6. Hydrolytic degradation of 73PBA6.9P at 85 °C. Lines by integration of indicated equations with k_0 = 0.9 × 10^{-6} equiv/(g·day), k = 0.26 day^{-1}, and k' as indicated in g/(equiv·day). (△, —) $\Delta(M_n^{-1})$; (▲, ---) [A]; (◭, ---) [P].

supplies randomly placed acid groups continuously.

Another complicating factor is that two molecules of polyester acid that have reacted with the same carbodiimide molecule have been coupled together. To obtain evidence of this, samples used in studying the dry reaction[4] which had orginally contained large amounts of A and P were run on the gel chromatograph. In a sample aged 3.8 days at 85 °C, M_n had increased from 12 000 to 20 000 and the weight-average molecular weight had increased from 53 000 to 93 000. After 4 weeks at 85 °C, values of M_n and the weight-average molecular weight were 32 000 and 150 000, respectively.

Figure 6 shows results obtained with 73PBA6.9P at 85 °C in wet aging. Experimentally, the rate of disappearance of carbodiimide decreases after 24 days and measurable carbodiimide remains when $\Delta(M_n^{-1})$ and [A] are high, suggesting that the apparent k' indeed changes. Our calculation, which is little more than curve fitting, starts with k_0 = 0.9 × 1.0^{-6} equiv/(g·day), k = 0.26 day^{-1}, and k' = 4 × 10^4 g/(equiv·day). The initial value of k' from ref 4 is 1.6 × 10^4, but if this value is used, [A] gets so high that the calculated carbodiimide content decreases more rapidly than observed. With k' = 4 × 10^4 g/(equiv·day), $-d[P]/dt$ between 1 and 24 days is nearly equal to k_0. Thus a value of k_0 that is only about 20% less than that found for 73PBA4.9M fits the P data well at times less than 24 days. Times after 24 days show results of two calculations, one with k' = 4 × 10^4 and the other with k' suddenly reduced to 100 g/(equiv·day). The reduction in apparent k' gives a fairly good fit to the carbodiimide data but predicts an earlier rapid rise in $\Delta(M_n^{-1})$ and [A] than observed. A still smaller k' would improve the fit to P data but would make fits to $\Delta(M_n^{-1})$ and A data worse.

Qualitatively similar results were obtained with polymer 66PCL6.0P at 85 °C. Two values for k' accommodated P data but the change to the smaller k' caused early discrepancies between observation and calculation for $\Delta(M_n^{-1})$ and A. For these k_0 = 0.9 × 10^{-6} equiv/(g·day), k = 0.19 day^{-1}, and k' = 4 × 10^4 g/(equiv·day) throughout gave reasonable fits, for example, predicting 10^{-4} (mol of scissions)/g at 41 days whereas this was found at 46 days. At 62 days no carbodiimide remained and the acid content was 125 × 10^{-5} equiv/g. Thus all P is available at 85 °C if there is a large excess of acid.

Table III
Degradation at 55 °C, 100% Relative Humidity, with Polycarbodiimide

time, days	10^5[A], equiv/g	10^5[P], equiv/g	$10^5\Delta(M_n^{-1})$, (mol of scissions)/g
	Polymer 73PBA6.9P		
0	0.2	5.3	0
54		5.1	-0.1
116	0.1	5.1	1.0
184	0.2	4.2	1.6
241		3.9	2.7
281		3.7	3.1
375		3.1	2.3
478	2.9	2.9	3.3
600	55	0	53
	Polymer 66PCL6.0P		
0	0.7	4.3	0
70		3.4	0.3
131	0.7	3.0	-0.1
209	0.3	2.5	1.1
291		2.1	0.4
367		1.7	1.9
448	2.6	1.5	4.5
569	24	0	22

Results obtained with polymers 73PBA6.9P and 66PCL6.0P at 55 °C are in Table III. In the next to last time interval the decrements in the P contents are very small. [A] is also moderately large despite the presence of similar amounts of P, so the apparent k' had decreased as at 85 °C. Presumably, k_0 should equal the rate of disappearance of P after consumption of the initial acid but before the apparent k' decreased, which the data suggest happened at about 370 days. Therefore, values of k_0 were calculated from $([P_0] - [A_0] - [P_t])/t$, where t is equal to 370 days. The values equal 0.5 × 10^{-7} equiv/(g·day) for both polymers, slightly less than calculated from the rate of disappearance of M at 55 °C. The disappearance of P in the last time interval presumably comes about because the small effective k' no longer limits [A], which increases by reaction 4 to levels which consume P.

At 35 °C changes in M_n after 475 days are not significant in polymers 73PBA6.9P and 66PCL6.0P. Values of [A] were determined after 125 days and found to be 0.2 × 10^{-5} and 0.4 × 10^{-5} equiv/g, respectively. Values of [P] after 475 days are 4.8 × 10^{-5} and 3.0 × 10^{-5} equiv/g, respectively. The k_0, calculated at $([P_0] - [A_0] - (P_{475}])/475$, are 0.6 × 10^{-8} and 1.3 × 10^{-8} equiv/(g·day), respectively. These values are not significantly different because of the small changes in [P]. Their arithmetic mean, 10^{-8}, agrees well with the value deduced from the disappearance of M, 1.1 × 10^{-8} equiv/(g·day).

Activation Energies. There are not significant differences in k_0 between PBA and PCL polymers or in those found by use of P instead of M. Consequently, the activation energy was calculated from the arithmetic mean k_0 at each temperature, i.e., 1.0 × 10^{-8} equiv/(g·day) at 35 °C, 6.0 × 10^{-8} equiv/(g·day) at 55 °C, and 1.0 × 10^{-6} equiv/(g·day) at 85 °C. By least squares the activation energy is 85 ± 5 (standard error) kJ/mol. The activation energy of k is about 65 kJ/mol; values for k' are 53 and 82 with M and P, respectively, this last being for the initial k'.[4]

Discussion

With monocarbodiimide the mechanism describes the data reasonably well. If the initial [M] substantially exceeds $[\mathrm{A}_0]$, k_0 determines the rate of destruction of M and hence the lifetime of the stabilized polymer. To a good approximation this lifetime can be calculated by linear extrapolation of observed carbodiimide contents starting from $([\mathrm{M}_0] - [\mathrm{A}_0])$ at time zero to the time at which [M] equals zero and then adding the lifetime of unstabilized polymer. One significant result of the uncatalyzed hydrolysis is that chain scission occurs at rate k_0 even if a large amount of carbodiimide is present. This is observed in all our results.

Uncatalyzed hydrolysis of esters is an accepted process. It is of interest to compare a rate constant for this process with our k_0. For ethyl acetate in water the rate constant at 25 °C for the uncatalyzed hydrolysis is given as 2.5×10^{-10} s^{-1}.[6] This value includes the water concentration, about 0.05 equiv/g,[7] giving 5×10^{-9} g/(equiv·s) when calculated as a second-order rate constant. Extrapolation of the k_0 data to 25 °C gives $k_0 = 2.2 \times 10^{-12}$ equiv/g·s). This includes the ester content, about 10^{-2} equiv/g, and the water content, about 0.5 wt % or 3×10^{-4} equiv/g. Thus as a second-order rate constant our k_0 is equivalent to 7×10^{-7} g/(equiv·s), more than 100 times the value for ethyl acetate. This seems a very large effect to attribute to differences in ester structure or media, although the latter are extreme. However, the tendency of water to cluster to polymers may make its bulk concentration a poor indicator of its chemical activity. If water in the polymer behaves locally as bulk water, then our k_0 can be divided by the ester content, giving 2.2×10^{-10} s^{-1}, and this divided by the fraction of ester groups associated with the clusters. Presumably, this fraction is small, perhaps less than 0.1, giving 22×10^{-10} s^{-1}, to be compared with 2.5×10^{-10} s^{-1} for ethyl acetate. Furthermore, our current studies with poly(ester diols) and M appear to give values of k_0 only 20% of those found in the polyurethanes at 85 °C, suggesting some influence of the urethane group.

Alternative mechanisms were considered and rejected for various reasons. Reactions 4 and 5 without reaction 3 are not adequate because they predict that very quickly [A] will approach zero and [M] will become approximately equal to $[\mathrm{M}_0] - [\mathrm{A}_0]$. The rates of chain scission and of disappearance of carbodiimide will then be nil and the polymer should last forever. Such behavior is not observed.

Another possibility is that hydrolysis might be catalyzed by something not reactive with carbodiimide; i.e., k_0 in reaction 3 could as well be the product $k''[\mathrm{C}]$, where [C] is the concentration of a residual esterification catalyst, a catalyst for the urethane reaction, or some derivative thereof. However, essentially the same values of k_0 are obtained for a polycaprolactone- and two poly(butylene adipate)-based polymers. One of the latter was made commercially and the other was made without a catalyst in our laboratory. Generally, polycaprolactone esters are made by opening a ring under basic conditions whereas poly(butylene adipate) esters are made by the tin or titanium alkyl ester catalyzed reaction of acid and alcohol. It seems unlikely that the three values of $k''[\mathrm{C}]$ could be so nearly the same when different catalysts are involved.

A third possibility is that after reaction with A_0, carbodiimide disappears by a process first order in [M] instead of zero order in [M], the data for the present argument being regarded as too imprecise to distinguish first from zero order. Carbodiimide is known to react with water in the presence of 0.1 N perchloric acid by a first-order process[8] and one cannot be sure that a catalyst for carbodiimide hydrolysis is not in our polymers. However, the values of k' in reaction 5 are such that [A] would be driven to extremely low values while the carbodiimide was being consumed in the first-order process. Since scissions would only be caused by reaction 4, they would not increase uniformly with time as observed. Also, once [A] is very small it increases very slowly by reaction 4 when M is exhausted, making predicted lifetimes at 85 °C several times those observed.

A fourth possibility is that the acylureas formed in reaction 5, hereafter D, are themselves hydrolyzed to acid and urea. This mechanism may be written

$$-\mathrm{CO_2}- + \mathrm{H_2O} \xrightarrow[\mathrm{A}]{k} -\mathrm{CO_2H} + \mathrm{HO}- \tag{4}$$

$$\mathrm{A} + \mathrm{M} \xrightarrow{k'} \mathrm{D} \tag{5}$$

$$\mathrm{D} + \mathrm{H_2O} \xrightarrow{k''} \mathrm{A} + \text{urea} \tag{9}$$

The initial acid will be consumed quickly by (5); then [A] will take on a steady-state concentration given by

$$[\mathrm{A}] = k''[\mathrm{D}]/k'[\mathrm{M}]$$

from which

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k''[\mathrm{D}]$$

$$\mathrm{d}\Delta(M_\mathrm{n}^{-1})/\mathrm{d}t = kk''[\mathrm{D}]/k'[\mathrm{M}]$$

The quantity of D will not change rapidly since it is formed by (5) and destroyed by (9); hence $k''[\mathrm{D}]$ will be what we call k_0. Since $k/k'[\mathrm{M}]$ is usually much less than unity, scissions will occur much less rapidly than M is consumed, contrary to most of the observations.

It is clear from the foregoing that the slow but steady accumulation of scissions in the presence of M is an important observation, since it helps eliminate several possible mechanisms.

The situation with the insoluble polycarbodiimide is too complex to expect successful analysis. At 85 °C, P is about as effective as M despite k' being initially smaller for the former and becoming smaller still as the reaction proceeds. It is tempting to attribute this to the cross-linking capability of P. Since k_0 is a property of the polyester, values should be the same in the presence of either carbodiimide as observed.

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