Structure and Reaction Mechanism for the Monoacid Diol Polyester from Caprolactone and 2,2′-bis(Hydroxymethyl)propionic Acid: NMR and Melting-Point Evidence

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ABSTRACT: The product distribution in the synthesis of acidic hydroxypolyesters from a 6/1 mol ratio of caprolactone and 2,2′-bis(hydroxymethyl)propionic acid (DMPA) changes with reaction time and temperature. ^{13}C-nuclear magnetic resonance (NMR) signals were identified that are specific for all the possible substitution products around the quaternary carbon in the DMPA. This allows quantitative determination of the six different species that are present. NMR studies showed that over one-half of the product is substituted on only one of the DMPA hydroxyls. The residual DMPA concentration increases at times and temperatures higher than those required to just complete caprolactone conversion because of equilibration of the kinetic product. All process conditions produced polyesters with two melting points. This suggests that the monosubstituted and disubstituted families of oligomers which are present are not completely miscible with one another. Polyester melting points increase as reaction time and temperature increase. This indicates that the degree of polymerization of the polycaprolactone arms increases as the severity of the preparative condition increases.
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INTRODUCTION

The monoacid diol polyester that can be prepared by the reaction of caprolactone with 2,2′-bis(hydroxymethyl)propionic acid (DMPA) is useful in the preparation of aqueous urethane dispersions.[1] More recently, this polyester has been used in the synthesis of graft copolymers for use as pigment dispersants by reacting it with a 2,3-epoxypropyl methacrylate/*n*-butyl methacrylate copolymer. The preparation of the polyester was unexpectedly complicated.[2] The polyester formed two phases when it was melted and stored at 60°C, the acid number depended on the severity of the reaction condition, and all products had two melting points which varied with the preparative condition. Scriven and Chang[1] prepared the polyester by heating a mixture of caprolactone and DMPA for 4.5–6 h at 125 to 150°C. At the shorter time and lower temperature, conversion of caprolactone was only 89.6%. The rapid reaction of caprolactone with DMPA to complete conversion at 2 h × 120°C observed in this work, as well as the complexity of the reaction, would not be expected from the work of Scriven and Chang.

NMR was used to provide detailed quantitative information about the composition of the polyester produced under different conditions. This information also was used along with melting-point

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and fractionation studies to deduce the degree of polymerization of the caprolactone arms produced under various reaction conditions.

EXPERIMENTAL

Materials Used

DMPA and dibutyltin dilaurate (DBTDL) were purchased from Aldrich (Milwaukee, WI). Caprolactone was obtained from the Union Carbide Corp. (Danbury, CT). Their Tone® monomer EC, HP was used without purification. As supplied, this material is at least 99.8% caprolactone. It contains less than 0.05% water and has an acid number of less than 0.3.

Analytical Methods

Acid Number Determination

ASTM D 1639, "Test Method for Acid Value of Organic Coating Materials," was used. Because the methods of synthesis for the polyesters described in the discussion produces monoacid functionality, a number-average molecular weight can be calculated directly from the acid number by dividing 56,100 by the acid number. Based on the repeatability of this titration, the molecular weight is estimated to be within ± 2% of the calculated value, for example, $MW = 1000 \pm 20$.

Differential Scanning Calorimeter Method for Polyester Melting-Point Determination

A TA Instruments 2920 DSC was used. The heating rate was 10°C/min. in a N_2 atmosphere from −80 to 150°C. The 10-mg samples were cooled at the same 10°C/min rate back down to −80°C and reheated to 150°C. The melting points from the second scan are reported in the Results and Discussion section. This procedure assured that the samples had a similar short-term heat history.

Molecular Weight by Size-exclusion Chromatography

The standards used were polystyrene of 3.04M, 1.03M, 330K, 156K, 66K, 28.5K, 9.2K, 3.25K, and 580 molecular weight. A point-to-point calibration was used with these narrow molecular weight standards. Tetrahydrofuran was used as the solvent. A Waters 410 RI detector was used for the measurements. The columns used were from Poly Laboratories (part # 1110-6500). The column heater temperature was 30°C. The detector temperature was 35°C. The flow rate was 1.0 mL/min with an injection volume of 100 μL of the 0.1% solution of experimental polymer in tetrahydrofuran. The samples were filtered through a 0.5-μm Millipore filter before being run.

^{13}C-NMR

^{13}C-NMR spectra were obtained on a 400-MHz Varian NMR spectrometer on 20 wt/vol % solutions of the mixture in DMSO-d_6 in a 10-mm NMR tube using a spectral width of 35 kHz, an acquisition time of 0.45 s, a recycle delay time of 30 s, and a 90-degree pulse. Repeats of some samples were run with a 45-s recycle delay. A line-broadening value of 3.5 Hz was used and the spectra were zero-filled to 128K before integration. Spectra were obtained at 30°C except for the highest melting-point sample of DMPA/caprolactone adduct, which was run at 60°C because it was not soluble at 30°C. The NMR run time was about 24 h for each sample. Samples were heated to 60°C and mixed and vortexed thoroughly before taking the 620-mg NMR sample.

The T_1's were measured for the ^{13}C-NMR signals of the monomer DMPA at 20 wt % in DMSO-d_6 at 30°C. The longest T_1 was 8.1 s for the peak at 49.5 ppm. Thus, the NMR data obtained on the higher oligomers using a recycle delay of 30−45 s and an acquisition time of 0.45 s should be quantitative. The data obtained on the same sample run with a 30-s recycle delay and a 45-s recycle delay were identical within the error of our ability to integrate these signals.

The ^{13}C-NMR results have a relative accuracy of 5% for larger peaks and of 20% for smaller peaks. However, the precision, especially with a single experienced operator doing integrations, is much better than that. The ^{13}C-NMR results have a relative precision of 1% for larger peaks and 5–10% for smaller peaks [see Fig. 6(B)]. Precision is least accurate, of course, for the lowest S/N peaks. In determining the trend of a series of samples, the precision is more important than is the absolute accuracy. An extra significant figure was retained in cases where ratios of peaks were taken to more clearly identify trends in a series of samples.

Polyester Synthesis Examples

Uncatalyzed Reaction of Caprolactone with DMPA, 6/1 Mol Ratio

This polyester was prepared by heating 106.4 g of DMPA with 543.6 g of caprolactone in a stirred

reactor under dry nitrogen. The mixture was heated with stirring over 50 min to 115°C. Heat was turned off after the solution cleared at 115°C and the reaction had become exothermic. Over the next 10 min, the exotherm carried the mixture to 120°C. Heating was resumed to keep the temperature at 120°C for 2 h. The product contained 99.6% nonvolatile and had an acid number of 69.8 (theory, 68.5). Upon cooling, it was an opaque soft white wax. It showed two melting points, 5.3 and 26°C, in the second scan at 20°/min in a differential scanning calorimeter. ^{13}C-NMR analysis indicated that 43.1% of the product molecules have both OH's modified with caprolactone, about 46.9% have 1 OH modified, and the product contains about 10% of the charged DMPA with no modification. No esterification of the carboxyl group of the DMPA was detected. When the reaction was scaled up, the exotherm caused the temperature to overrun 120°C. For example, when the charge was four times as large, the temperature reached 140°C and the acid number was 68.3, indicating that esterification had begun. External cooling was not used in either preparation. The impact of different times and temperatures of the reaction on product characteristics is described in the Results and Discussion section.

DBTDL-catalyzed Reaction of Caprolactone with DMPA, 10/1 Mol Ratio

Caprolactone, 1141.5 g (10 mol), DMPA 134.1 g (1 mol), and 1.7 g of a 10% solution of DBTDL in xylene was charged to a nitrogen-blanketed reactor fitted with a stirrer, thermocouple, and reflux condenser. This quantity of DBTDL, 133 ppm on reactants, corresponds to 25 ppm tin in the reactants. During heat up, the heat was cut at 125°C and the exotherm was used to carry the reaction to 150°C. The mixture was heated at 150°C for 4 h to completely polymerize the caprolactone. When cooled, the product was an opaque white solid. The product contained 99.3% nonvolatile and had an acid number (solids basis) of 43.0. The theoretical acid number was 44, indicating that 2.3% of the carboxyl content of the polymer had been esterified. The M_n calculated from the acid number was 1300. The M_n found by SEC (PS standards) was 3370. Several other mol ratio products were made by this procedure (see Table I in the Results and Discussion section).

Table I DMPA/Caprolactone Adducts

CL to DMPA Mol Ratio, n	M_n Calculated from Stoichiometry	M_n Calculated from Acid No.	SEC M_n, Polystyrene Standard
4	591	680	1940
6	819	890	2340
10	1276	1330	2880
15	1846	1870	3890
25	2988	2820	6650

RESULTS AND DISCUSSION

Stoichiometry, Catalysis, and Reaction Conditions

Initially, the reaction of caprolactone and DMPA was considered to be adequately represented by Figure 1. The polyester was made in a number of ratios of caprolactone to DMPA as shown in Table I. All these materials were made by heating the reactants for 4 h at 150°C with 133 ppm of DBTDL on the reactants as the catalyst. All the products were white solids. This was the reaction condition that had been previously observed to be necessary to cause caprolactone to completely react with primary diols such as 1,6-hexanediol and was 15°C lower than the temperature needed to complete the uncatalyzed 1,6-hexanediol reaction in 4 h.

The M_n's calculated from the acid numbers were 14.5% higher to 5.6% lower than expected from the stoichiometry. The variation was systematic from the lowest stoichiometry to the highest, indicating that esterification of the DMPA carboxyl was important when the DMPA concentration was high and was less important above n = 10. The material with a CL/DMPA ratio of 4

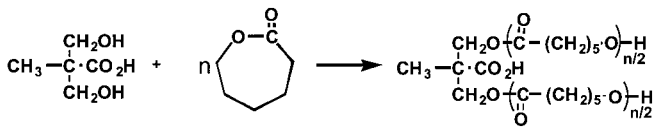

Figure 1 Hydroxyl-containing monocarboxylic acid polyester.

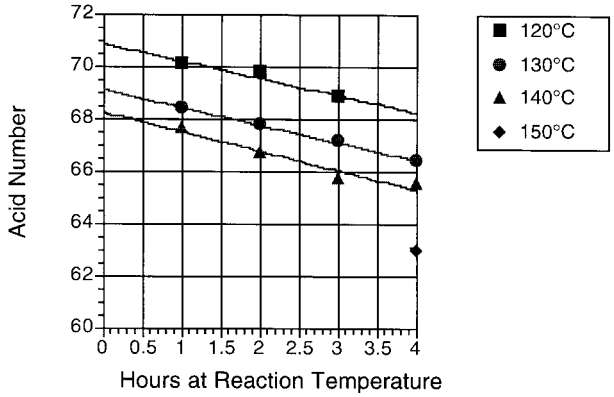

Figure 2 Esterification is a side reaction at 120, 130, 140, and 150°C.

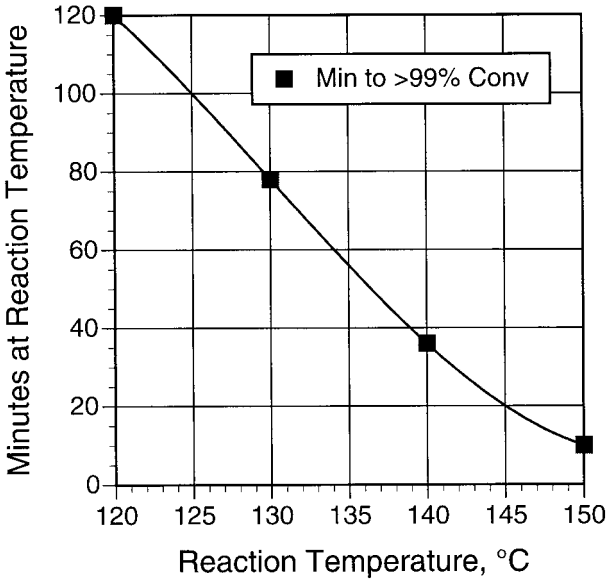

Figure 3 Time at reaction temperature to get >99% caprolactone conversion in the uncatalyzed reaction of 6/1 caprolactone/DMPA.

did not form a clear melt at 100°C, suggesting the presence of residual DMPA. Graft copolymers[2] containing the $n = 10$ adduct slowly crystallized from the solution. This led to the major part of the work being done with the $n = 6$ adduct. As the reaction was investigated in more detail, it was found that the 6/1 adduct could be prepared at 120°C in 2 h in the absence of a catalyst (see Experimental section, Uncatalyzed Reaction of Caprolactone with DMPA, 6/1 Mol Ratio). This indicates that the carboxyl group in the DMPA is a catalyst for the caprolactone ring-opening reaction. Small decreases in acid number from the theoretical value of about 68.5 occurred at higher temperatures, as shown in Figure 2.

The time to convert the caprolactone to a polymer in the self-catalyzed process is very temperature-dependent, as described in Figure 3, which shows the time required, after about 60 min heat up from 22°C, to give >99% conversion of the caprolactone. The conversion of the caprolactone during the heat up was between 23% (120°C) and 98% (150°C). The conversion figures were calculated by assuming the volatile loss during the gravometric solids determination at 2 h at 105°C was due to the loss of unpolymerized caprolactone.

NMR Characterization of the Reaction Products

^{13}C-NMR was used to determine the type and distribution of products present in the samples as a function of the reaction conditions. Figure 4 shows several substitutions that can form by reaction of the hydroxyl and acid groups of DMPA. Figure 5 shows the ^{13}C-NMR spectrum and the assignments for sample 3a, the product made in the self-catalyzed reaction at 2 h × 120°C. Figure 6 compares the quaternary carbon region (42–57 ppm) of sample 3a with the same molar composition made with DBTDL catalysis at 4 h × 150°C. The quaternary carbons are labeled according to the scheme in Figure 4. The assignment of resonance M0 was confirmed by spiking the sample with the DMPA monomer. M1, M2, and M3 were assigned by studying the highly branched self-condensation product of DMPA. In this product, M1 and M3 must be equal in intensity; the signal at 50 ppm is assigned to M1 as it has a sharper

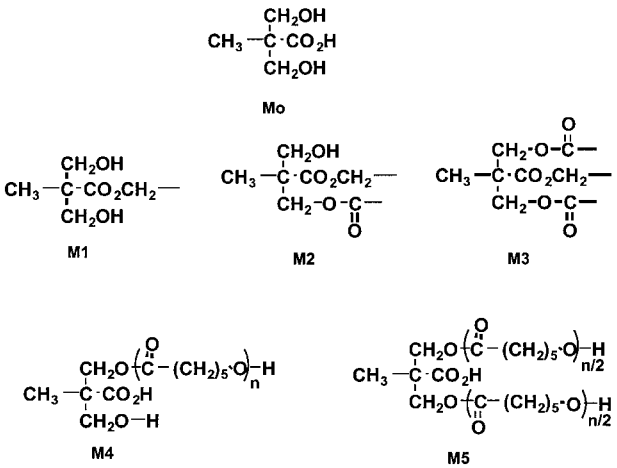

Figure 4 Substitution pattern for DMPA and caprolactone.

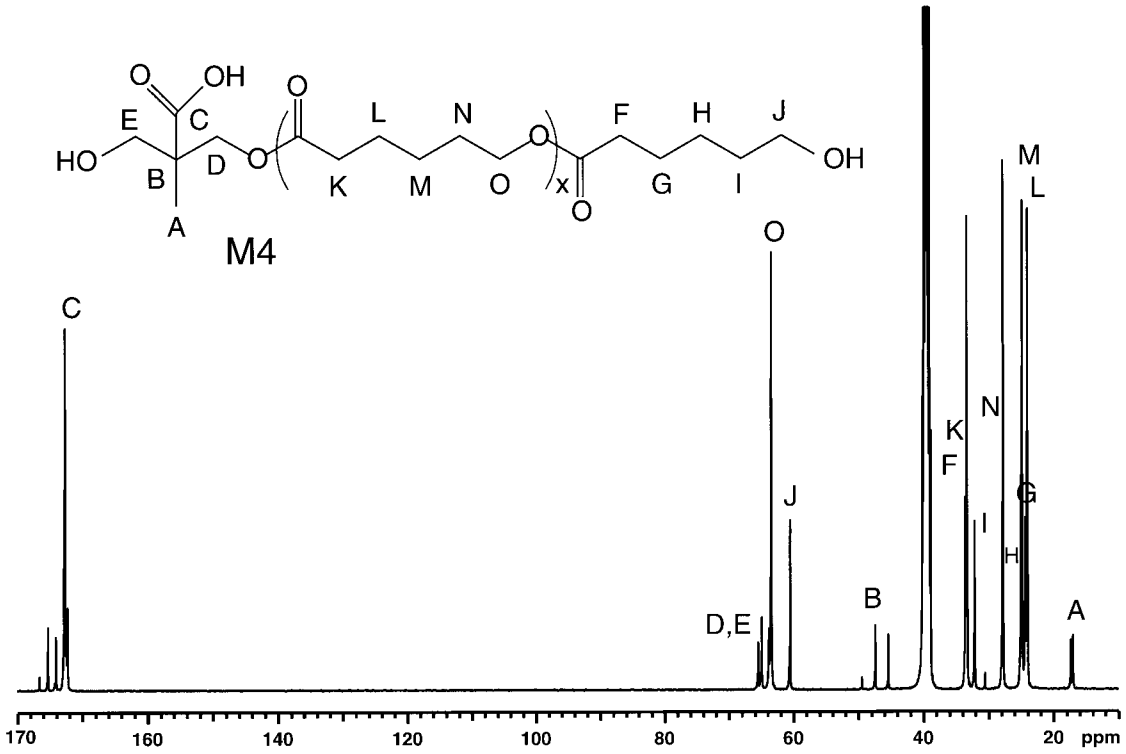

Figure 5 M4 structure and NMR peak assignments.

signal than has the peak at 46.0 ppm; the symmetry of structure M1 should give rise to a sharper resonance for M1 than for M3. This is also consistent with the shift difference between M0 and M1 due to conversion of the acid to an ester (see below). M2 is easily assigned in the self-condensation product of DMPA as it has a greater intensity than has M1 or M3. Our assignments are completely consistent with those of Malmstrum and coworkers,[3] who assigned these peaks based on a series of model compounds. For the sample shown in Figure 6(B), the signals M1, M2, and M3 are shifted from M0, M4, and M5 by a consistent amount due to the esterification of

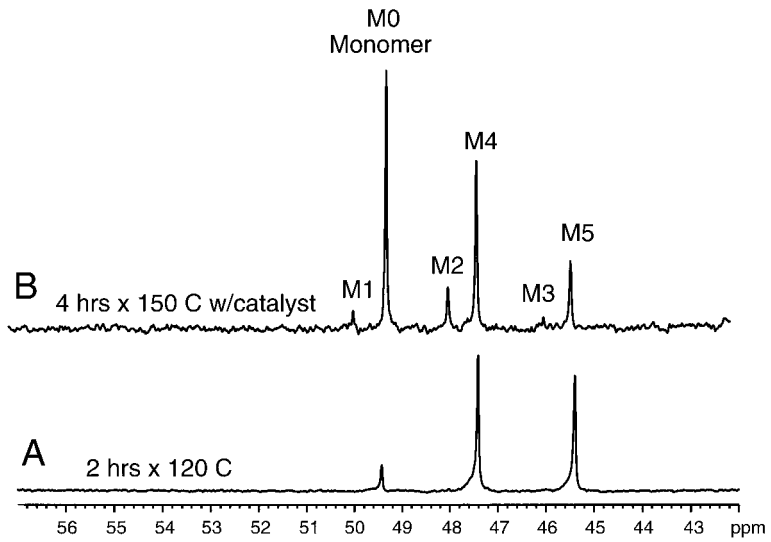

Figure 6 ^{13}C spectra of two polyesters differing in residual DMPA content.

Table II Product Distribution in Caprolactone/DMPA (6/1) Reaction, Mol % of Charged DMPA in the Species in Figure 4

Reaction Condition	M0	M1	M2	M3	M4	M5	M4/M5
10 min at 150°C	8.4		0.8	trace	47.2	43.6	1.08
1 h at 120°C (97% Caprolactone conv.)	9.3				47.9	42.7	1.12
2 h at 120°C	10				46.9	43.1	1.09
4 h at 120°C	10.9				49.3	42.9	1.15
4 h at 130°C	15.0	1.4	2.2	2.1	47.3	32.0	1.48
4 h at 140°C	14.2	2.1	4.7	1.3	48.3	29.4	1.64
4 h at 150°C	15.6	2.2	5.9	2.8	45.9	27.6	1.66
4 h at 150°C with 133 ppm DBTDL	43.5	3.6	7.6	2.3	31.0	12.0	2.58

M0 to M5 are described in Figure 4. M0 is unmodified DMPA. M4 is the monoester acid. M5 is the diester acid.

the central acid group, supporting a self-consistent set of assignments. It is also logical that the NMR resonance for M4 would be more intense than that for M5 and M0 at low-to-moderate ratios of caprolactone to DMPA in the reaction. The relative amounts of M0, M1, M2, M3, M4, and M5 structures in these samples were obtained by integration of these quaternary carbon signals in the region 45–51 ppm. This should give quantitative results based on the conditions used and the T1 data measured for the DMPA monomer. Carbonyl resonances for M0, M4, and M5 are observed at 176.6, 175.3, and 174.0 ppm. Carbonyl resonances for M1 and M2 are tentatively assigned to the peaks observed at 174.6 and 173.4 ppm. The free acid carbonyl of caproic acid or the acid end of polycaprolactone is observed at 174.2–174.3 ppm; this assignment was confirmed with an authentic sample of polycaprolactone run under the same conditions. The ^{13}C resonance of the free—CH2OH end of caproic acid or polycaprolactone is at 32 ppm. No residual caprolactone (resonance at 68.4 ppm) was observed in any of the samples.

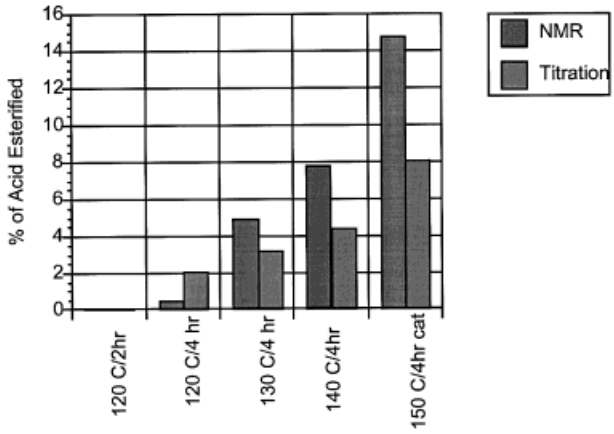

Figure 7 Esterification of DMPA carboxyl can occur without loss of acid titer.

Table II describes how the distribution of the six substitutions shown in Figure 4 of caprolactone on DMPA changes with the preparative condition. One of the most surprising observations from Table II is that more of the charged DMPA is present after the more vigorous reaction conditions than at the minimum reaction condition required to convert the caprolactone. This has the important consequence that a uniform melt is produced when the 2 h × 120°C product is melted, while the material made at 4-h heating at 150°C with the DBTDL catalyst produced a melt that rapidly formed two layers. The layering is probably because this product contains 43.5% of the initially charged DMPA without any attached caprolactone, and this leads to a higher degree of polymerization of the caprolactone arms. The insolubility of the DMPA and the high acid number oligomers with only one hydroxyl modified would be more pronounced under this circumstance.

Table III Melting Behavior of Polyesters Made at Increasing Reaction Times at 130°C

Hours at 130°C	Exo of Rcst. J/g	Mp 1	Mp 2	Mp 2 Endo J/g	Acid No.
1	36.0	6.2	27.5	51.0	68.4
2	3.2	10.6	31.9	50.5	67.8
3	0.9	14.1	34.3	54.1	67.2
4	0	17.2	36.2	52.2	66.4

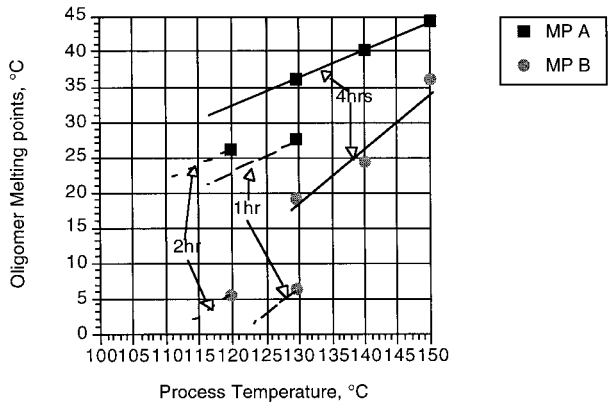

Figure 8 Caprolactone/dimethylolpropionic acid 6/1 oligomers, melting point versus process time and temperature.

Either one alcohol of the DMPA (M4 in Table II and Fig. 4) or both alcohols (M5 in Table II and Fig. 4) are substituted. There is a trend to a higher ratio of the singly substituted oligomer to the doubly substituted oligomer at higher reaction temperatures (M4/M5 ratio in Table II) and, of course, both decrease as the free DMPA acid content increases and as esterification of the carboxylic acid occurs. Evidently, DMPA is reforming at the expense of both mono- and di-substituted oligomers. Redistribution of the lower melting caprolactone oligomer to form higher melting oligomers was described by Domeier and Hsi for other diols.[4] They emphasized the use of low levels of a catalyst and minimum reaction conditions needed to get caprolactone conversion to avoid caprolactone redistribution.

NMR can also detect esterification of the DMPA carboxyl group. Titration results are compared to NMR results in Figure 7. There is no esterification at the lowest reaction condition, 2 h at 120°C, but there is increasing esterification as reaction conditions become more severe. NMR results are for M1 + M2 + M3, whereas acid titration includes all sources of acid (including small amounts of CL ring opening by adventitious water).

Table V Melting Points of Whole and Fractions from 120°C × 2-h Polyester

Sample	First MP (°C)	Second MP (°C)
Whole	5.3	26.0
Top	27.7	40.1
Bottom	14.7	34.4

The increasing difference between the titration and NMR results after the 120°C × 4 h sample indicates that there is a reaction that esterifies DMPA carboxyl groups which does not result in an overall loss of acid content. This reaction is probably the attack of the DMPA acid group on an ester to form esterified DMPA with the liberation of a new carboxyl group. The reaction does not involve caprolactone because it does not become significant until after all the caprolactone is consumed. As was discussed above, a new carboxylic functionality similar to the group in caproic acid, that is, with the carboxyl next to a series of methylene groups, was detected by NMR. The reaction of a carboxylic acid with an ester to form a new acid is referred to as "acidolysis."[5] Acidolysis is used to make half-acid esters, for example, by reacting diethyl adipate with adipic acid. It is used to make vinyl esters by reacting carboxylic acids with vinyl acetate.[6] The mechanisms involved were discussed.[7] The synthetic procedures for "acidolysis" often involve lower temperatures, about 100°C, and similar times to those used in the current study. They have been optimized by using traces of strong acids as catalysts. In the case of vinyl ester preparation, mercury salts are also used. It is believed that the results reported above are consistent with "acidolysis" with weak acid catalysis driven by the higher temperature (to 140°C) used in these studies.

In summary, the carboxyl group of DMPA is a catalyst for caprolactone ring opening, leading to complete conversion of caprolactone in as little as 2 h at 120°C. More vigorous reaction conditions lead to esterification and equilibration of the ki-

Table IV Fractionation of the 6/1 Polyester made at 2 h × 120°C

Layer	%	Acid No.	M0	M1	M2	M3	M4	M5
Top, toluene-soluble	45.8	52.3	4.0	ND	trace	trace	52.0	44.0
Bottom, toluene insoluble	54.2	64.7	4.0	ND	0.4	1.2	58.8	35.6
Unfractionated polyester			10				46.9	43.1

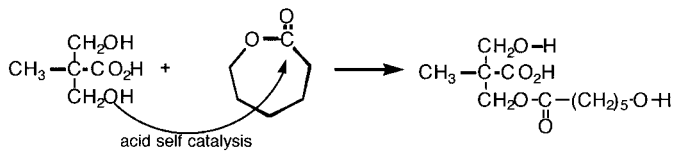

Figure 9 Exothermic reaction of caprolactone with DMPA.

netic product to a mixture containing more free DMPA. As the temperature and time increase, acidolysis occurs to a minor extent. Even the product formed under the least severe condition, 2 h at 120°C, contains less than half of the DMPA with caprolactone substitution on both hydroxyls.

Melting Behavior of the 6/1 Caprolactone/DMPA Polyesters

The melting behavior of the adducts was unexpected in two ways: As the severity of the reaction conditions decreased, the melting point decreased. Further, there were two distinct melting points for each sample.

It is particularly instructive to follow the changes in the melting-point behavior that occurred as a function of time (1, 2, 3, 4 h) at 130°C. All samples were previously heated at 10°C/min to 150°C and recooled to −80°C at the same rate prior to this melting cycle to provide a uniform heat history.

Table III shows the behavior of samples taken from the 130°C reaction mixture at 1, 2, 3, and 4 h. The 1-h sample shows similar melting behavior to the material described in the Experimental section as being made with 2 h heating at 120°C. Particularly, note the crystallization exotherm (Exo of Rcst. J/g) that occurs in the 1-, 2- and 3-h samples. As the melting points of the polyester increase, there is less supercooling with accompanying crystallization as the sample is remelted. This is probably the consequence of the formation of longer polycaprolactone chains with increasing reaction time due to equilibration of the kinetic product. Mp 1 and Mp 2 increase monotonically. The endotherm for Mp 1 is only about 15% of the endotherm for Mp 2. The endotherm for Mp 2 is approximately the same for all samples. There is a modest trend downward in the acid number, indicating that esterification occurs even at 130°C.

Figure 8 describes the melting-point behavior as a function of reaction time and temperature. Complete caprolactone conversion was obtained after 1 h at 130°C and the melting points were similar to those seen with material made at 120°C for 2 h.

The decrease in melting points as the reaction time and temperature are decreased is due to the formation of more, but shorter, polycaprolactone units under the less severe conditions. The degree of polymerization (d.p.) of the arms in the 2-h at 120°C sample is estimated to be 4.4 and the 4-h at 150°C run with DBTDL catalysis to be 7.4. This estimate is based on the consumption of hydroxyl and carboxyl groups of DMPA from the NMR data in Table II. The difficulty with this approach is that at other temperatures the change in calculated d.p. of the intermediate products from 4.4 to 4.9 does not seem sufficient to account for an increase in melting point from about 25 to 40°C. There is probably also a redistribution to a mixture of arms containing longer arms. The generally accepted melting point[8] of high polymer (d.p. >100) polycaprolactone at atmospheric pressure is 60°C although values as high as 69°C have been reported.[9] The highest observed melting point in this study, 45°C, is consistent with a d.p. of about 10 for the arms.

The possibility that the dual melting points are caused by separate crystallization of the two families of oligomers, one monosubstituted, the other disubstituted, was investigated by fractionation of one of the polyesters. Dilution of 1 part of the 2 h × 120°C product with 9 parts of toluene produced a toluene-soluble layer, a toluene-insoluble layer, and a sediment which was probably DMPA.

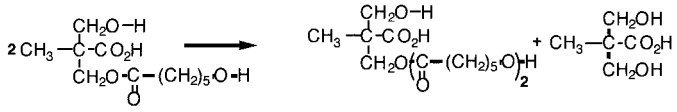

Figure 10 Polyester equilibration by ester interchange.

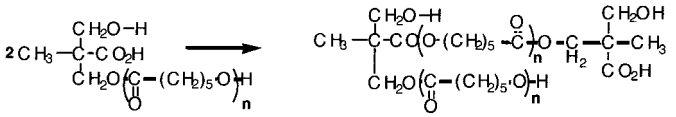

Figure 11 Acid loss by direct esterification.

Table IV shows the composition of the materials recovered from the two layers. The toluene-soluble material contains more caprolactone, as indicated by the lower acid number, and more of the disubstituted product, M5. The mechanical loss of DMPA on the bottom of the vessel is evident as the starting sample contained about 10 mol % of the DMPA as unsubstituted material and these fractions contained only 4%. Both fractions still showed two melting points, which were higher than were the melting points of the original sample (see Table V). The original sample has lower melting points than either of the fractions obtained by toluene extraction. Since the original sample is a mixture of the two fractions, its lower melting point corresponds to a reduction in the purity of one material by the other. This mixed melting-point behavior (melting-point depression) supports the theory that the two families of oligomers are causing the two distinct melting points and that they are partly soluble in one another so give the melting-point depression observed in the whole sample. The higher melting points in the toluene soluble ("top") sample is consistent with this material containing runs of caprolactone that are longer than are those in the bottom (toluene-insoluble) fraction.

Mechanism of Polyester Formation, Esterification, and Redistribution

The initial reaction mixture is a slurry of DMPA in caprolactone. By the time the mixture reaches 115°C, all the DMPA has gone into solution. At that point, about 24% of the caprolactone (by weight) has reacted. At the outset, only the hydroxyls of the DMPA are present to react with caprolactone. This exothermic reaction is probably acid-catalyzed by the high concentration of carboxylic acid in the mixture, as illustrated in Figure 9. This is the main reaction until appreciable caprolactone is consumed. After caprolactone-derived hydroxyls are available, the reaction with caprolactone can proceed both on the newly formed hydroxyl and the residual DMPA hydroxyls. The NMR study indicates that the newly formed hydroxyls are more reactive. In the 2 h × 120°C product, over half of the originally present hydroxyls from DMPA are not consumed.

The second most important reaction is hydroxyl/ester interchange, which is also an acid-catalyzed process (Fig. 10). The hydroxyls from caprolactone are more reactive than are those from DMPA, as indicated by the accumulation of DMPA under more vigorous reaction conditions and the reduced amount of the product with both DMPA hydroxyls substituted under the more severe reaction conditions. This reaction accounts for the growth of the longer, higher melting polycaprolactone arms under the more vigorous reaction conditions.

The third most important reaction is the direct esterification of hydroxyls by the DMPA acid group (Fig. 11). The hydroxyls are most likely those from the caprolactone, which are the most available/reactive of the two.

Finally, the least common reaction is that of the carboxyl group of the DMPA with an ester to form a new ester with the ejection of an arm fragment containing a carboxyl group (Fig. 12). This results in the esterification of the DMPA carboxyl without overall loss of the carboxyl content of the polymer.

Note added in proof: The NMR results that were interpreted to show that acidolysis is occurring could actually be showing that polyester arms are being hydrolyzed by water being formed in the primary esterification process. If acidolysis is occurring, it probably is not by the direct reaction described in Figure 12, but through a lactone or anhydride intermediate.

CONCLUSIONS

The product distribution in the synthesis of acid hydroxypolyesters from a 6/1 mol ratio of capro-

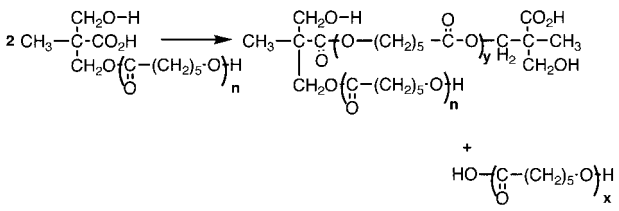

Figure 12 Acid/ester interchange.

lactone and DMPA is dependent on reaction time and temperature. The simplest product, free of esterification of the DMPA carboxyl and containing a minimum amount of DMPA, was made by running the reaction at 120°C for 2 h.

^{13}C-NMR peaks were identified that are specific for all the possible substitution products around the quaternary carbon in the DMPA. This allows quantitative determination of the six different species that are present. NMR studies show that over half of the reaction product is substituted on only one of the DMPA hydroxyls. The residual DMPA concentration increases at times and temperatures higher than those required to just complete caprolactone conversion because of equilibration of the kinetic product. This reequilibration is particularly evident when DBTDL catalysis is used. All process conditions produced polyesters with two melting points. This is thought to be because the monosubstituted and disubstituted families of oligomers which are present are not completely miscible with one another. A fractionation study supports this hypothesis.

Polyester melting points increase as reaction time and temperature increase. This indicates that the degree of polymerization of the polycaprolactone arms increases as the severity of the preparative condition increases. The arms are estimated to reach a degree of polymerization of at least 10 even though the simplest stoichiometry predicts a maximum of arms with a degree of polymerization of 3.

T. J. Dushanko prepared the caprolactone adducts. The NMR data were obtained by M. J. Halfhill. The thermal analysis was done by M. Y. Keating. The authors are grateful to D. Ovenall for some of the initial NMR assignments and to C. Urbsten for producing the NMR figures. C. B. Douglas reviewed the manuscript and made helpful mechanistic suggestions. Y. H. Kim suggested the explanation for the melting-point behavior of these polyesters.

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