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Direct polyesterifcation in aqueous emulsion

M. Baile, Y. J. Chou, and J. C. Saam*

The Dow Corning Corporation, Midland, MI 48686-0995, USA

Summary

Certain diols can undergo polycondensation in aqueous emulsion with either dicarboxylic acids or aliphatic aldehydes to give polyesters or polyacetals. The process occurs under mild conditions and requires water insoluble liquid monomers, the presence of a sulfonate surfactant and mobile cations which can ion exchange at the oil-water interface. An acidic catalyst is not necessary. The degrees of polymerization are modest but they exceed those normally expected of polyesterifcations in such an environment. The driving force is thought to be the heat of condensation of the water produced as vapor in the oil phase.

Introduction

Reversible polycondensations proceeding through the elimination of water are typically conducted so that the produced water is in some way removed continuously from the system in order to favorably shift the equilibrium. In apparent contradiction to this it was found that silanol ended polydimethylsiloxane oligomers in aqueous emulsion stabilized by sulfonic acid surfactants could eliminate water spontaneously and condense to high polymers (1). The polymerization proceeded under mild conditions and molecular weights at equilibrium were inversely dependent on temperature. A principal driving force was suggested to be the heat of condensation of water produced as vapor in the dispersed silicone oil phase to water as liquid upon its transport to the aqueous phase. Evidence was offered that the polymerization occurred at or near the oil-water interface and certain similarities with surface catalysis were pointed out. These findings are now extended to the polycondensation of diols with dicarboxylic acids or aliphatic aldehydes in aqueous dispersion(2),(3).

Examples of polycondesation in aqueous media include interfacial condensation or phase transfer catalysis to form polycarbonates(4), polyesters or polyamides(5), self amidation of surface active amino acid esters in the air-water surface film to form polypeptides(6) and the reaction of triethyl oxonium fluoroborate with carboxylates to form esters(7). All produce unwanted by-products such as chloride ion, carbinols, boron halides, etc. Although direct polyesterifcation would avoid this, examples have not been found in the literature despite the potential advantages of such a process. One possible exception is an early claim of forming polyspirane resins in aqueous solution or suspension from dialdehydes and pentaerythritol in the presence of acids or acidified lauryl sulfate surfactants(8). Molecular weights in the region of 2000 were reported. While the products lacked rigorous characterization, the examples cited suggest that direct polycondensation in aqueous media might be possible. Potential advantages in such a process include the avoidance of organic solvents and mild conditions.

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*To whom offprint requests should be sent

Experimental Section

The dicarboxylic acids, aldehydes, diols and acid anhydrides were obtained from the Eastman Kodak Company. The surfactants were from the Stephan Chemical Company. GPC molecular weights were determined on a Waters 440 GPC using Styragel columns and THF.

Procedure for Evaluation of Catalysts and Surfactants. Azelaic acid, 32.4 g., (0.17 mole) and 1,10-decanediol, 30.0 g. (0.17 mole) were dispersed in 100 ml. of water containing the specified amounts of surfactants and catalysts in Table 1. The systems usually emulsified spontaneously after brief stirring at 75°, but within 48 hrs. at this temperature the emulsions tended to coagulate, particularly if there was significant conversion of the monomers. At this time the mixtures were cooled and the polymers isolated and analyzed. The water was evaporated at room temperature and the residual solids were further dried at room temperature for 24 hrs. in a vacuum prior to any analysis. Equivalent weights were determined by titration of the unpurified product with excess standard sodium hydroxide followed by back titration with standard hydrochloric acid. Equivalent weight was calculated according to equation 1 when an acidic surfactant was present.

1. $$\text{Eq. Wt.} = [1000\,(1 - x)\,W] / [N\,(V - x\,W/NE)]$$

where x is the weight fraction of acidic surfactant or catalyst used, W the weight of sample, N the normality of titrant, E the equivalent weight of acidic catalyst or surfactant and V the volume of titrant at the end point. Equivalent weights measured in this fashion agreed roughly with number average molecular weight (M_n) measured in a few examples by GPC, Table 1. The insoluble fraction in methanol was determined by shaking the dried powdered product in 25 ml. of methanol for two hrs. and separating the insoluble polymer by centrifugation. The precipitate was dried at room temperature and atmospheric pressure and then for 24 hrs. in vacuum at room temperature.

Evaluation of Monomers. Monomers which could be successfully polymerized by this procedure were evaluated by essentially the same technique. An equimolar mixture of the diol and dicarboxylic acid (35 g.) in question was dispersed at 60-70° in 65 ml. of a 0.7% aqueous solution of dodecylbenzenesulfonic acid (DBSA). The emulsion was held at the temperature specified in Table 2 for 48 hrs. Equivalent weight was determined on the unpurified product.

Poly(12-hydroxystearic acid). A mixture of 200 g. of 12- Hydroxystearic acid (0.666 mole), 1.1 g of DBSA, 46 g. of toluene and 500 ml. of water was heated to 85-90°. The toluene served to depress the melting point of the acid. The resulting suspension was passed three times through a heated Manton Gaulin homogenizer at 6000 p.s.i. while being held at least at 70° to give a stabile emulsion. A 400 ml. portion of the emulsion was refluxed gently with stirring at 99° while the toluene was distilled from the system. This was continued over a period of 8 days and samples were periodically removed to determine neutral equivalent and to monitor progress. At the end of this period the equivalent weight of the unpurified product was 979 while that of the methanol extracted polymer was 1902.

Poly(decamethylene maleate). A mixture of 34.8 g. of 1,10-decanediol (0.200 mole), 19.6 g. of maleic anhydride (0.200 mole) and 2.2 g. of DBSA was heated at 80-90° for 0.5 hr. then 150 ml.. of water was added with stirring. The system emulsified spontaneously and the temperature was adjusted to 23° in one portion and to 75° in a second equal portion. Samples were taken intermittently and equivalent weights were determined on unpurified product. At 23° the emulsion destabilized after 5 hrs. and equivalent weight had increased from an initial value of 360 to 2320. There was no destabilization at 75° and equivalent weight had decreased from an original 525 to 277 after 18.5 hrs. Data are graphed in Figure 1.

Poly(decamethylene phthalate). A mixture of 30.0 g. 1,10-decanediol (0.172 mole), 25.6 g. of phthalic anhydride (0.172 mole) and 2.6 g. of DBSA was heated at 70° for 0.5 hr. As soon as the mixture was completely molten 130 ml. of water was added with stirring and the system spontaneously emulsified. The emulsion was divided into two equal parts and temperature was adjusted to 23° in one and 80° in the second. Equivalent weights were then determined on unpurified samples periodically taken to trace the progress of the polymerizations. At 23° the equivalent weight increased from 331 to 1975 after 24 hrs. and

Table 1.
Catalysts and Surfactants for the Polymerization of 1,10-Decanediol and Azelaic Acid in Aqueous Emulsion

Catalyst/Surfactant (weight, g.)	% Methanol Insoluble	Equivalent Wt. (g./ equiv.) Unpurified [a]	 Purified [b]	GPC Mn	 Mw
Non-surface active Acidic Catalysts					
None	0	251	------	------	------
HCl (37%, 10.0)	44	673	940	------	------
H_3PO_4 (85%, 7.2)	24	753	871	728	1330
H_2SO_4 (4.0)	65	2606	3588	3000	5950
CF_3SO_3H (4.0)	78	1066	1540	------	------
TOSH[c] (4.0)	59	909	1466	------	------
Surface Active Acidic Catalysts					
$MeC_{10}H_6SO_3H$ (4.0)	82	1767	2094	------	-----
$ROSO_3H$[d] (30%, 1.54)	41	483	1200	------	------
DBSA[e] (2.0)	76	1099	1889	------	------
$R_2C_{10}H_5SO_3H$ (7.0)	66	836	3236	------	------
$R'NMe_3Cl$[f]/HCl (4.0/4.0)	0	-----	------	------	------
$R'NMe_3Cl$/ H_2SO_4 (4.0/4.0)	45	1749	3475	------	------
$R'NMe_3SO_4H$ (10.0)	72	1101	1487	------	------
Makon10[g]/H_2SO_4(1.5/4.0)	71	1423	2794	1790	3220
NaDBSA/ TOSH (2.0/4.0)	---	1346	-------	1810	4020
Non-acidic Catalysts					
$ROSO_3Na$ (2.0)	24	447	722	------	------
NaDBSA[h] (2.0)	64	1740	2296	------	------
Sodium sulfated-methyl oleate (3.5)	50	1296	2097	------	------
$R'NMe_3SO_4Na$/-Na_2SO_4 (10/3.9)	46	394	632	------	------
$R'NMe_3SO_4Na$ (10.0)	0	------	------	------	------
$(R'NMe_3)_2SO_4$	0	------	------	------	------
$R'NMe_3Cl$ (3.0)	0	------	------	------	------
Makon 10 (1.5)	0	------	------	------	------

a. Determined on the dried emulsion prior to washing in methanol. b. Determined after washing the product in methanol. c. p-Toluenesulfonic acid. d. R = $C_{12}H_{25}$. e. Dodecylbenzenesulfonic acid.
f. R' = $C_{16}H_{33}$. g. Makon 10 = $C_{12}H_{25}C_6H_4(C_2H_4O)_{10}H$. h. Sodium dodecylbenzenesulfonate.

the emulsion had destabilized, while at 80° equivalent weight decreased from 331 to 269 and the emulsion remained stabile (Figure 2).

Poly(oxy/decamethyleneoxy-n-heptylidene). Mixtures of 17.4 g. of 1,10-decane-diol (0.10 mole), 11.4 g. of heptaldehyde (0.10 mole) and the amounts of catalysts and surfactants specified in Table 3 were dispersed in 130 ml. of water. The resulting emulsions were heated first at 50° for 1 hr. and then at 23° for 24 hr. By this time coagulation was obvious in the examples where polycondensation had occurred. The systems were then adjusted to a pH of 7-8 with 0.1 N aqueous sodium hydroxide and the organic phases were separated. These were washed with methanol and the insoluble products were separated and dried in a vacuum at room temperature. Yields and molecular weights are reported in Table 3. Infrared spectra of the polymers showed absorptions at 2920, 2855, and 1460-1470 cm.$^{-1}$

Table 2
Influence of Temperature and Diol Water Solubility on Equivalent Weight

Carbinol	Acid	Polymerization Temperature(°C	Equivalent Wt. (g./ equiv.)
--------------	12-hydroxystearic	97	1084
1, 10-decanediol	Azelaic	25	300
1, 10-Decanediol	Azelaic	65	1240
1, 10-decanediol	Azelaic	97	1120
1,6-hexanediol	Azelaic	65	722
Ethylene glycol	Azelaic	65	120
Ethylene glycol	Azelaic	0-65	90-100

Table 3
Polycondensation of Heptaldehyde with 1,10-Decanediol

Catalyst or Surfactant (g.)	% Insoluble in Methanol	GPC Mn
DBSA (1.0)	64.7	2890
DBSA (1.0)[a]	4.0	2290
NaDBSA(1.1)[b]	61.8	2820
H_2SO_4 (1.7)	48.5	2860
None	0.0	-------

a. The emulsion was not neutralized prior to extraction with methanol. b.Sodium dodecylbenzenesulfonate.

due to CH_2, and at 1130 to1110 cm.$^{-1}$ and 1050 cm.$^{-1}$ characteristic of ether linkages. Absorptions corresponding to carbonyl were absent. ^{1}H NMR (CCl_4) d 0.9 (t, 3H), 1.3 (m, 26H), 3.5(t, 4H), 4.5 (t, 1H).

Discussion of Results

The most effective catalysts in promoting the polycondensations were either the sulfates or sulfonates and of these sulfuric acid appeared to be the most efficient, Table 1. It can also be seen in Table 1 that, with exception of sulfuric acid, some degree of surface activity was important for efficient catalysis. Sulfuric acid might owe its effectiveness to *in situ* formation of an amphophilic sulfate ester of the water insoluble diol. The activity of some of the other non-surface active acids could be explained in the same way. The cationic quaternary ammonium surfactant promoted polymerization only when the latter could associate with bisulfate counter ions and when the mobile cations H^+ or Na^+ were present. This could be achieved with the hexadecyltrimethylammonium chloride surfactant when bisulfates or sulfuric acid were dissolved in the water phase . These presumably ion exchange at the oil-water interface with the chloride associated with the cationic surfactant . The cationic surfactant alone with sulfate or chloride as a counterion did not promote polymerization and its presence as a chloride completely suppressed the minimal activity seen with hydrochloric acid alone.

Surprisingly acidity did not appear to be an important criterion for effective catalysis and the sodium salts of some of the sulfonate surfactants promoted polymerization as well as their acidic counterparts. A modest reaction was even noted when the catalyst system consisted of sodium sulfate in combination with the cationic surfactant associated with a sulfate anion. Nonionic surfactants were ineffective but when present they did not appear to interfere seriously with other active catalytic species.

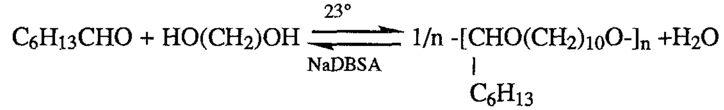
All of the surfactants surveyed failed to stabilize the emulsion as the reaction progressed and coagulation was usually noticed as molecular weights approached 2000. After this the polymerizations ceased or were retarded. Since long chain carbinols are well known cosurfactants(9), the unreacted 1,10-decanediol may well be contributing to emulsion stability and its consumption during polymerization could ultimately lead to coagulation. Thus it was uncertain if the observed molecular weights represented the polymerization at equilibrium or simply a point at which the polymerization terminated due to coagulation.

Only monomers insoluble in water polymerized. If either the diol (Table 2) or the dicarboxylic acid were soluble in water there was no polymerization. In addition to the examples in Table 2 it was shown that maleic, fumaric and glutaric acids, all water soluble, would not undergo polymerization. It was also important that the mixture of monomers in the dispersed phase be liquid during polymerization and it was necessary to adjust temperature or add small amounts of solvent to insure that the dispersed phase remained liquid. Thus it was necessary to include initially a small amount of toluene in the polymerization of 12- hydroxy-stearic acid. This monomer polymerized at a much slower rate than the others, probably because of its less reactive secondary carbinol. No polymerization was seen in an equimolar mixture of phthalic acid and 1, 10 - decanediol which was solid up to 100°C.

The water soluble dicarboxylic acids, which themselves were incapable of emulsion polymerization, could be incorporated into the emulsion polymers as low molecular weight water insoluble oligomers of the diol. Dispersion of the crude oligomers in water in the presence of DBSA resulted in polymerization provided the emulsions were held at room temperature. The same technique also allowed the incorporation dicarboxylate structures where the corresponding diacids were found unreactive because of their high melting points. Examples are shown in Figures 1 and 2 where 1,10-decanediol was first partly esterified with maleic or phthalic anhydrides in the presence of DBSA and then emulsified. The data also illustrate the importance of low temperature for successful polymerization with this type of monomer. In the case of poly(decamethylene maleate) the polymerization completely reversed when the temperature was increased from 23° to only 50°C. The result qualitatively resembled the reversible polycondensation of silanol ended oligomeric polydimethylsiloxanes in aqueous emulsion where molecular weights were also inversely dependent on temperature.

The polyacetal from n-heptaldehyde and 1,10-decanediol formed in emulsion under conditions similar to those employed for the polyesters to give polymers with molecular weights between 2000 and 3000 (Equation 3). The various catalysts surveyed are listed in Table 3. Care was taken when DBSA was present to insure that the system was neutral prior

3.



$$C_6H_{13}CHO + HO(CH_2)OH \underset{NaDBSA}{\overset{23°}{\rightleftharpoons}} 1/n\ \text{-}[\underset{\substack{|\\ C_6H_{13}}}{CH}O(CH_2)_{10}O\text{-}]_n + H_2O$$

to washing the crude product with methanol because of the polymer's sensitivity to acid catalyzed solvolysis. Otherwise the process was as simple and straightforward to conduct

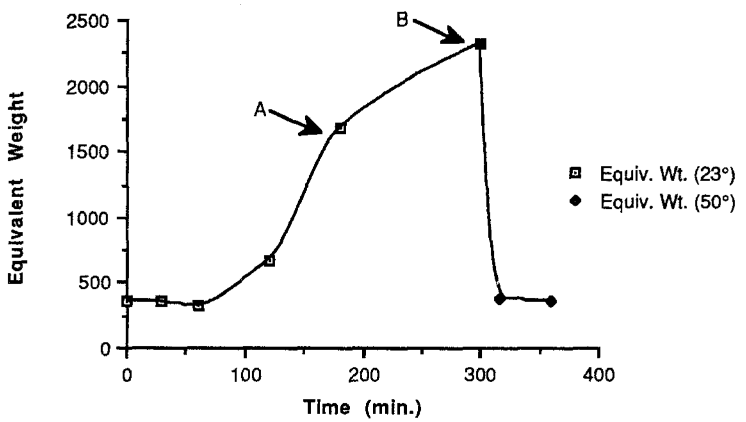


Figure 1. Polyesterification in aqueous emulsion of the oligomers made in a prior step by warming in bulk equimolar maleic anhydride and 1,10-decanediol in the presence of DBSA. Water was added at 30 min. Destabilization of the emulsion was noted at point A. Temperature was changed from 23° to 50° at point B.

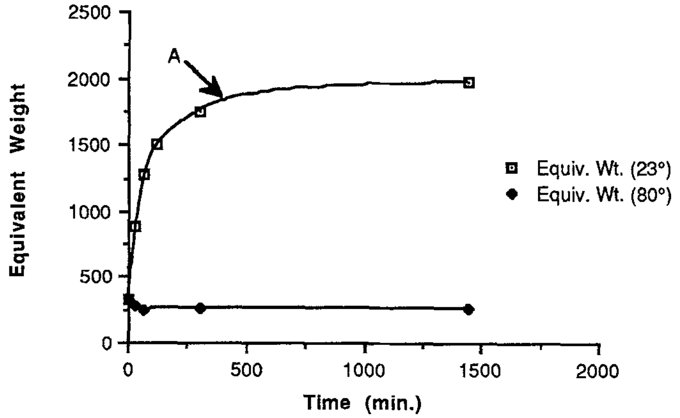


Figure 2. Polyesterifcation in aqueous emulsion of the oligomers made in a prior step from warming in bulk equimolar phthalic anhydride and 1,10-decanediol in the presence of DBSA. Water was added after 30 min. Polymerization temperatures 23° upper curve, 80° lower curve. Point A indicates where destabilization of the emulsion was noted.

as the polyesterifcation. The sodium salt of DBSA was one of the most effective catalysts and its use avoided the acid catalyzed side reactions sometimes encountered in preparing this type of polymer. Benzaldehyde and 1,10-decanediol, however, failed to polymerize by this method. Typically polyacetals are made in the presence of strongly acidic catalysts while continuously removing water at elevated temperatures in a refluxing hydrocarbon(10).

Conclusions

The observations qualitatively resemble those made on the reversible silanol polycondensation in emulsion (1) and a mechanism for removal of the produced water from the site of the reaction is also required here. Molecular weights in the present system of only 500-600 would be anticipated, for example, if all the produced water in the dispersed oil phase where participating in the equilibrium and there were not some process for its removal from the site of the reaction. To explain this water is pictured as existing as a gas in the dispersed oil phase where its amount is controlled by its solubility and vapor pressure at the temperature of the polymerization. Subsequent transport of the gaseous water to the aqueous phase would then amount to its conversion to the liquid state with an attendant release of about 10.5 kcal./mole, a significant contribution to the overall driving force.

A possible,but not necessarily exclusive, mechanism for the transport of water from the site of reaction is a cycle where cations associated with the surfactant in the dispersed oil phase can expand their sphere of hydration with the water produced in the polymerization. The surfactant with its more highly hydrated cation then migrates to the oil-water interface to undergo exchange with cations at other states of hydration. The more hydrated cation, locating ultimately in the aqueous phase, would eventually be replaced by one at a lower state of hydration and return to the oil phase with a surfactant anion where the cycle would repeat *ad infinitum* or until the sytem coagulates. Mobility would be required and a liquid dispersed phase with surfactants associated with cations capable of movement would be critical. This was qualitatively in agreement with observation.

The ability of the sodium salts of the sulfonate surfactants as well as their acidic forms to act as catalysts cannot be reconciled with the classical mechanism for acid catalyzed polyesterifcation(11). To account for this it is proposed that the reaction proceeds through a sequence where the long chain carbinol can associate with the sulfonate surfactant and then form a sulfonate or sulfate ester. The tendency of long chain carbinols to associate with sulfonates is reported(12) and sulfonate esters are well known reagents for the alkylation of carboxylates(13). The sulfonate ester is therefor proposed to be the key intermediate in forming the ester linkage. The sequence in reactions 3, 4 and 5 below is a schematic representation of the proposed process where R and R' represent aliphatic groups and X is the hydrophobic group of the surfactant.

3. $$\mathrm{ROH + XSO_3^- \rightleftharpoons [ROH, XSO_3^-] \rightleftharpoons ROSO_3X + OH^-}$$

4. $$\mathrm{R'CO_2H + OH^- \rightleftharpoons R'CO_2^- + H_2O}$$

5. $$\mathrm{ROSO_3X + R'CO_2^- \rightleftharpoons R'CO_2R + XSO_3^-}$$

A similar sequence, where the hydrated aldehyde or hemiacetal from the aldehyde and the diol would replace the carboxylate, could apply to the formation of polyacetals.

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