[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Formation of a Cyclic Recurring Unit in Free Radical Polymerization. II[1]

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Cyclic recurring units are formed in the free radical catalyzed polymerization of α,α′-dimethylenepimelonitrile. The polymer prepared from the corresponding amide was not soluble in any solvent which was tried, but it is not certain whether this is caused by crosslinking or by the highly hydrogen bonded structure of the polyamide. Some observations on the copolymerization behavior of the diolefin derivatives have been recorded. Dimethyl α,α′-dimethyleneadipate can be polymerized to give recurring units containing a five-membered ring. This appears to be less easily accomplished than is to cyclization in the pimelate series.

The formation of a cyclic recurring unit in the free radical polymerization of α,α′-dimethylenepimelic acid (Ia) and its esters (Ib) has been reported recently.[2] We have now extended this investigation to include the polymerization reactions of α,α′-dimethylenepimelamide (Id), α,α′-dimethylenepimelonitrile (Ie), as well as some of the copolymerization reactions of these two monomers with several simple acrylic-type comonomers. Dimethyl α,α′-dimethyleneadipate was also investigated to determine the ease of formation of a five-membered ring in a free radical polymerization reaction.

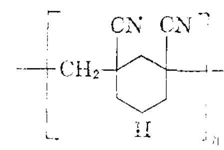
$$CH_2{=}\overset{R}{\overset{|}{C}}(CH_2)_3\overset{R}{\overset{|}{C}}{=}CH_2$$

Ia, R = CO_2H
b, R = $-CO_2CH_3$, $-CO_2C_2H_5$
c, R = $COCl$
d, R = $CONH_2$
e, R = CN

α,α′-Dimethylenepimelonitrile (Ie) was prepared from the corresponding pimelic acid (Ia) derivative. α,α′-Dimethylenepimelic acid was converted to the acid chloride (Ic) with thionyl chloride and then to the amide by the action of cold concentrated ammonia in an over-all yield of 80%. Dehydration was effected in a 62.5% yield by treating a pyridine solution of the amide with benzenesulfonyl chloride at moderate temperatures. Dimethyl α,α′-dimethyleneadipate was prepared by a series of reactions similar to those used for the preparation of the pimelate.[2]

α,α′-Dimethylenepimelonitrile polymerized in dimethylformamide solution and in emulsion systems to produce a polymer which was soluble in hot dimethylformamide and which had an inherent viscosity of 0.655. The infrared spectrum indicated that a small amount of the monomer units was incorporated by a non-cyclic process and the remaining double bonds are hanging from the chain; however, the spectral and solubility data were in agreement with the cyclic structure II as the major recurring unit of the polymer.

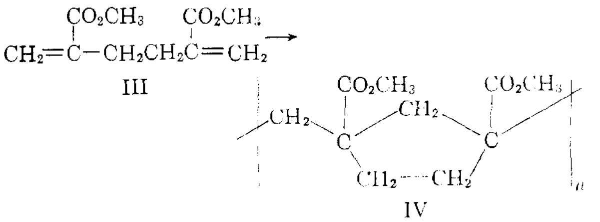
Poly-α,α′-dimethylenepimelonitrile did not change color until heated to temperatures above 275°. This is in sharp contrast to the thermal stability of polymethacrylonitrile which undergoes thermal discoloration at 140°.[3] Poly-α,α′-dimethylenepimelonitrile turned red at 300° and jet black at 325° over a period of three hours but the thermally degraded polymer contained about 80% of the original nitrogen content.



II

α,α′-Dimethylenepimelamide polymerized in dimethylformamide solution to yield, in high conversion, a polymer which is insoluble in the hot dimethylformamide solvent. The infrared spectrum of this polymer is not helpful in determining the amount of residual unsaturation because of the overlap of the amide carbonyl and carbon–carbon double bond absorptions; the terminal methylene absorption (928 cm.$^{-1}$ in the monomer) was not present in the polymer. It is possible that the amide nature of the polymer, rather than primary bond-crosslinking, rendered the polymer insoluble.

Dimethyl α,α′-dimethyleneadipate (III) polymerized in benzene solution to give a polymer which is soluble in benzene and chloroform and has an inherent viscosity of 0.21. A quantitative infrared analysis indicated that more than 90% of the monomer units were incorporated by a cyclic mechanism to produce a polymer containing a cyclic unit (IV) as the predominating recurring unit. Bulk or emulsion polymerization of this monomer gave only insoluble material for which the infrared spectrum showed two carbonyl absorptions of equal intensity corresponding to saturated and α,β-unsaturated ester. This datum indicated that the monomer units were not incorporated by a cyclic process under these conditions.



Dimethyl α,α′-dimethylenepimelate was originally reported[2] to polymerize in bulk solution or

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[2] C. S. Marvel and R. D. Vest, This Journal, **79**, 5771 (1957).

[3] N. Grassie and I. C. McNeill, *J. Polymer Sci.*, **27**, 207 (1958).

emulsion systems to give soluble polymers. A more extensive investigation of this reaction showed that the polymers produced in solution or emulsion are invariably soluble but those prepared in bulk polymerizations always contained some insoluble material. The soluble portion varied over a wide (5-95%) range and was apparently independent of variables such as initiator concentration and temperature.

Dimethyl α,α'-dimethylenepimelate copolymerized with acrylonitrile to produce a soluble polymer which had no residual unsaturation as indicated by its infrared spectrum. The analysis indicated a 65% incorporation of acrylonitrile in the copolymer and did not change on repeated purification.

α,α'-Dimethylenepimelonitrile copolymerized in emulsion systems with acrylonitrile and with methyl acrylate to produce predominantly insoluble materials. The copolymer of Ie and acrylonitrile was 7% soluble in hot dimethylformamide and the soluble portion possessed an unusually high inherent viscosity of 3.8. Analytical and spectral data indicated that the soluble and the insoluble fractions were identical in composition. The viscosity and solubility data suggest that the soluble portion may contain enough crosslinks to account for the high molecular weight but not enough to produce an insoluble polymer.

The soluble portion of the copolymer from methyl acrylate and the dinitrile amounted to only 2.2% of the charge and was a tough, elastic material. Neither fraction melted nor decomposed below 250°.

Experimental

α,α'-**Dimethylenepimelic Acid.**—The alkaline hydrolysis of diethyl α,α'-dimethylenepimelate was carried out by a procedure previously reported,[2] modified to minimize losses by polymerization. Under a blanket of nitrogen, diethyl α,α'-dimethylenepimelate[2] (96.0 g., 0.40 mole) was added dropwise to a stirred mixture of 400 ml. of 10% aqueous sodium hydroxide, 5.0 g. of sodium nitrite and 0.5 g. of freshly cleaned (washed with nitric acid) copper powder maintained at a temperature of 45–52°. After 24 hours at this temperature, the reaction was complete and the copper powder and polymer (3.0 g., 2.6%) formed were removed by filtration. The filtrate was then cooled and acidified to yield, after one recrystallization from water, 54.8 g. (74.5%) of α,α'-dimethylenepimelic acid, m.p. 103–104°. The melting point of the pure compound was 105.0–105.8°; however, for synthetic purposes, the product was not purified further.

α,α'-**Dimethylenepimelyl Chloride.**—This preparation was first tried on a 0.1-mole scale and then carried out on a 0.5-mole scale without modification. Under anhydrous conditions, redistilled thionyl chloride (35.7 g., 0.30 mole) was added dropwise *via* a dropping funnel over a period of 0.5 hour to dry, finely ground α,α'-dimethylenepimelic acid (18.4 g., 0.10 mole) while the reaction flask was warmed to 45–50° in a water-bath. Heating at this temperature was continued for an additional 0.5 hour and then gradually raised to 85–90° for an additional 1.5 hours. The flask was cooled somewhat and the volatile products and excess thionyl chloride removed under diminished pressure at room temperature. The crude acid chloride was not purified for analysis but used directly for the preparation of the amide below. An infrared spectrum[4] (smear) showed α,β-unsaturated acid chloride (1748 cm.$^{-1}$), carbon–carbon double bond (1631 cm.$^{-1}$) and terminal methylene (918 cm.$^{-1}$).

α,α'-**Dimethylenepimelamide.**—The crude α,α'-dimethylenepimelyl chloride (above) was cooled to 0° and poured slowly with rapid stirring into 300 ml. of concentrated ammonia, which was cooled to −10° prior to and during the addition. The ammonia solution was stirred for an additional 15 minutes and the product (14.5 g., 80% yield based on the diacid used) removed by filtration. A small sample, recrystallized five times from water, melted and rapidly polymerized at about 157°. A definite melting point could not be observed since, at that temperature, melting and polymerization proceeded simultaneously. The infrared spectrum (Nujol) showed α,β-unsaturated amide (1663 and 1607 cm.$^{-1}$), carbon–carbon double bond (1642 cm.$^{-1}$) and terminal methylene (928 cm.$^{-1}$).

Anal. Calcd. for $C_9H_{14}O_2N_2$: C, 59.32; H, 7.74; N, 15.37. Found[5]: C, 59.24; H, 7.78; N, 15.10.

α,α'-**Dimethylenepimelonitrile.**—The low temperature technique reported by Stephens, Bianco and Pilgrim[6] was used for the dehydration reaction. Under anhydrous conditions, a slurry of dry, finely ground α,α'-dimethylenepimelamide (36.4 g., 0.20 mole) and pyridine (80.2 g., 0.90 mole) was magnetically stirred at room temperature for 10 minutes; benzenesulfonyl chloride (70.6 g., 0.40 mole) was then added dropwise over a period of 1.25 hours. During this time the reaction temperature spontaneously rose to 48° and the mixture passed through a viscous stage and ended up as a clear tan solution. When the flask was heated on a steam-bath for 5 minutes, the pyridine hydrochloride formed in the reaction caused the mixture to solidify. The salt cake was transferred to 400 ml. of water and the product extracted with ether. The ether was removed and the product twice distilled under diminished pressure to yield a single fraction, m.p. 6–7°, b.p. 63–64° (0.04 mm.), $n^{20.0}_D$ 1.4708, d^{25}_{25} 0.94174. The yield was 18.3 g. (62.5%). Although the distillations were inhibited with clean copper wire, a small amount of insoluble polymer was removed from the pot after each distillation. The infrared spectrum (smear) of the pure monomer showed α,β-unsaturated nitrile (2230 cm.$^{-1}$), carbon–carbon double bond (1624 cm.$^{-1}$), terminal methylene (940 cm.$^{-1}$) and terminal methylene overtone (1885 cm.$^{-1}$). The ultraviolet spectrum (ethanol) showed an apparent λ_{max} at 201 mμ, ϵ_{max} 17,400.

Anal. Calcd. for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 73.95; H, 6.96; N, 19.33.

Tetramethyl 1,1,4,4-Butanetetracarboxylate.—According to the procedure reported for the preparation of tetramethyl 1,1,5,5-pentanetetracarboxylate,[2] dimethyl malonate (2592 g., 19.6 moles) and redistilled ethylene bromide (375.8 g., 2.00 moles) were condensed in the presence of methanolic sodium methoxide (92.0 g., 4.00 gram atoms, of sodium dissolved in 1500 ml. of anhydrous methanol). After removal of the excess dimethyl malonate, the product was isolated by crystallization and purified by two recrystallizations from methanol to yield white crystals, m.p. 77.6–78.4°, in a 259.0 g. (44.4%) yield. The infrared spectrum (chloroform solution) was typical of other malonic esters having a split carbonyl absorption (1730 and 1745 cm.$^{-1}$).

Anal. Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found C, 49.53; H, 6.25.

Dimethyl α,α'-**Dicarboxyadipate.**—The hydrolysis of tetramethyl 1,1,4,4-butanetetracarboxylate was accomplished by the procedure reported for similar compounds.[2] From 58.04 g. of the tetraester was obtained 48.0 g. (91.6%) of the pure diacid-diester. The reaction product was found to be analytically pure and melted at 114.0–116.0° (cloudy, decomposition with evolution of a gas observed). The infrared spectrum was consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{14}O_8$: C, 45.80; H, 5.83. Found: C, 45.91; H, 5.59.

Dimethyl α,α'-**Dimethyleneadipate.**—The Mannich reaction on dimethyl α,α'-dicarboxyadipate was carried out as described for the analogous pimelate[2] using diethylamine and aqueous formaldehyde (37%). Dimethyl α,α'-dimethyleneadipate, m.p. 26–27°, was isolated by crystallization from low boiling petroleum ether in 37% yield. The infrared spectrum (chloroform solution) showed α,β-unsaturated ester (1725 cm.$^{-1}$), carbon–carbon double bond (1633 cm.$^{-1}$), terminal methylene (947 cm.$^{-1}$), and terminal methylene overtone (1890 cm.$^{-1}$).

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(4) The infrared spectra were determined by Mr. P. McMahon and Miss Mary DeMott using a Perkin-Elmer model 21 spectrophotometer.

(5) The microanalyses were performed by Mr. Jozsef Nemeth, Miss Claire Higham and Mrs. F. Ju, University of Illinois, Urbana, Ill.

(6) C. R. Stephens, E. J. Bianco and F. J. Pilgrim, THIS JOURNAL **77**, 1701 (1955).

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.72; H, 7.33.

Poly-α,α'-dimethylenepimelonitrile. a. Emulsion Polymerization.—A charge of 5.00 g. of monomer, 5.0 g. of Office of Rubber Reserve soap solution, 1.00 ml. of thiophene-free benzene, 50.0 ml. of distilled water and 0.50 ml. of freshly prepared aqueous potassium persulfate solution (3%) was placed in a four-ounce polymerization bottle. After flushing with nitrogen, the bottle was capped and tumbled at 50° for 19 hours. The polymer was precipitated by pouring the emulsion into methanol and purified by dissolution of the polymer in hot dimethylformamide and reprecipitation in methanol. After drying for two days at 140° (0.1 mm.), 4.1 g. (82% conversion) of a white polymer having an inherent viscosity (0.235 g./100 ml. of dimethylformamide) of 0.655 was obtained. The infrared spectrum (Nujol) showed saturated nitrile (2238 cm.$^{-1}$), a small amount of unsaturation (1630 cm.$^{-1}$), but no absorption for terminal methylene. The polymer remained unchanged when heated to 275°, then gradually turned slightly tan between 275 and 300° and then black at 325°. A sample of the polymer heated to 310° for 3 hours lost 22.5% of the original nitrogen content.

Anal. Calcd. for $(C_9H_{10}N_2)_n$: C, 73.94; H, 6.90; N, 19.16. Found: C, 74.13; H, 6.82; N, 18.79.

b. Solution Polymerization.—In a two-ounce screw-cap polymerization bottle were placed 50 ml. of dry, redistilled dimethylformamide, 5.00 g. of monomer and 5.0 mg. of benzoyl peroxide. The bottle was then flushed with nitrogen, capped and placed in a constant temperature bath maintained at 55° for 15 hours. The soluble polymer was coagulated by pouring the polymerization solution into one liter of methanol to give 0.5 g. (10% conversion) of a white polymer which closely resembled in thermal properties the polymer prepared above. The infrared spectrum (Nujol) indicated saturated nitrile (2245 cm.$^{-1}$), but some unsaturation (1630, 950 cm.$^{-1}$).

Poly-α,α'-dimethylenepimelamide.—A two-ounce, screw-cap polymerization bottle was charged with 1.00 g. of monomer, 20 ml. of dimethylformamide and 10 mg. of benzoyl peroxide. The bottle was flushed with nitrogen, capped and placed in a constant temperature bath maintained at 60° for 24 hours. The polymer which formed during this time precipitated from solution. The suspension of polymer in dimethylformamide was rapidly stirred with 100 ml. of anhydrous methanol for 0.5 hour, removed by filtration and washed once with methanol, twice with ether, and dried under diminished pressure at 140°. The polymer (0.96 g., 96% conversion) was a white powder which did not melt after 2.5 hours at 250°. A sample immersed in the melting point bath at 170° showed no signs of melting, whereas, a sample of the monomer treated similarly melted quickly and then polymerized. The entire sample was neither dissolved nor swollen by hot dimethylformamide. The infrared spectrum (Nujol) showed typical absorptions for amide but no significant absorptions for unsaturation either in the carbon–carbon double bond or terminal methylene regions. Exhaustive washing of the sample failed to give a substance of analytical purity.

Anal. Calcd. for $C_9H_{14}O_2N_2$: C, 59.32; H, 7.74. Found: C, 58.59; H, 7.57.

In an attempt to emulsify the monomer, one emulsion polymerization was carried out with the addition of ethyl acetate to aid in emulsion formation. A charge of 5.00 g. of monomer, 35.0 g. of O.R.R. soap solution, 20.0 g. of ethyl acetate and 2.0 ml. of aqueous potassium persulfate (3%) solution was tumbled for 19.5 hours at 50° to yield 4.623 g. (92.5%) of a white polymer, essentially identical to that obtained by solution techniques. Hot dimethylformamide caused neither solution nor swelling of the polymer.

Anal. Calcd. for $C_9H_{14}O_2N_2$: C, 59.32; H, 7.74. Found: C, 59.89; H, 7.85.

Poly-dimethyl α,α'-Dimethyleneadipate. a. Solution Polymerization.—Under a blanket of nitrogen, 1.00 g. of monomer, 10.0 mg. of benzoyl peroxide and 25 ml. of thiophene-free benzene were heated under reflux for 7 hours. The clear solution was cooled and 0.25 ml. of a saturated solution of N-phenyl-β-naphthylamine was added to prevent further polymerization. The sample was frozen and the benzene sublimed to leave a semi-solid material which contained a considerable quantity of monomer. The sample was stirred with methanol to remove low molecular weight material and then reprecipitated twice by solution in benzene and precipitation in methanol. The final polymer was dissolved in benzene, frozen, and the benzene sublimed under diminished pressure to yield 180 mg. (18%) of a white polymer, m.p. 110–120°. Quantitative infrared analysis indicated that one double bond remained for every ten monomer units in the polymer. The inherent viscosity (0.34 g./100 ml. of benzene) was 0.21.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.49; H, 6.99.

b. Emulsion Polymerization.—A charge of 3.00 g. of monomer, 10.00 g. of water, 3.00 g. of O.R.R. soap solution and 0.50 ml. of a 3% aqueous potassium persulfate solution was placed in a 2-ounce polymerization bottle and the bottle flushed with nitrogen, capped, shaken for 5 minutes to emulsify the monomer and tumbled for 24 hours at 50°. The polymer was coagulated with a sulfuric acid–sodium chloride coagulant solution, removed by filtration and washed with methanol and then ether. The polymer (2.85 g., 95%) was dried under diminished pressure at room temperature. Infrared analysis indicated that only one double bond was involved in the polymerization reaction. The spectrum (Nujol) of the polymer showed absorptions for two ester carbonyls (1735 and 1720 cm.$^{-1}$, saturated and α,β-unsaturated ester, respectively) of approximately equal intensity, carbon–carbon double bond (1630 cm.$^{-1}$) but none for terminal methylene. The polymer was insoluble in benzene, *sym*-tetrachloroethane and chloroform, and did not melt below 250°. Removal of all impurities (presumably emulsifier) from the insoluble polymer was not achieved.

Anal. Calcd. for $(C_{10}H_{14}O_4)_n$: C, 60.59; H, 7.12. Found: C, 59.50; H, 7.13.

Copolymer of Dimethyl α,α'-Dimethylenepimelate and Acrylonitrile.—Dimethyl α,α'-dimethylenepimelate (2.12 g.) and acrylonitrile (4.77 g.) were copolymerized in an emulsion system at 50° to give 4.6 g. (67% conversion) of a white polymer which was soluble in hot dimethylformamide. The copolymer exhibited no definite melting point but decomposed rapidly above 180°. The analyses of the crude and purified polymer indicated that this was a true copolymer having 65% of the acrylonitrile incorporated. The infrared spectrum was essentially the same as that obtained by superimposing the spectra of the two homopolymers and showed no unsaturation. *Anal.* Found for unpurified polymer: N, 15.43; for purified polymer: N, 15.55.

Copolymer of α,α'-Dimethylenepimelonitrile and Acrylonitrile.—α,α'-Dimethylenepimelonitrile (1.00 g.) and acrylonitrile (14.9 g.) were copolymerized in an emulsion system at 50° and the polymer coagulated in a sulfuric acid–sodium chloride solution, dried and stirred with hot dimethylformamide for 24 hours. The soluble portion (1.4 g., 7.0%), having an inherent viscosity (0.222 g./100 ml. of dimethylformamide) of 3.8, was separated from the insoluble portion (13.3 g., 83.5%) by centrifugation of the hot dimethylformamide solution and subsequent precipitation of the individual fractions. The infrared spectra (Nujol) of both fractions were identical, showing some unsaturation at 1630 cm.$^{-1}$, and the analyses indicated that their compositions were the same. Both fractions decomposed around 250° but did not have well defined softening points. *Anal.* Found for insoluble fraction: N, 23.56; for soluble fraction: N, 23.93.

Copolymer of α,α'-Dimethylenepimelonitrile and Methyl Acrylate.—α,α'-Dimethylenepimelonitrile (1.0 g.) and methyl acrylate (19.0 g.) were copolymerized in an emulsion system at 50° and worked up as described for the above acrylonitrile copolymer, separating the soluble (0.43 g., 2.2%) from the insoluble (6.8 g., 34%) fractions by centrifugation of a suspension of the polymer in hot dimethylformamide. The soluble fraction was a clear, plastic material of considerable strength which did not melt or decompose below 250°; however, there was not enough material for complete characterization. The insoluble fraction was a gray solid which did not melt or decompose below 250°.

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