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Synthesis of Poly-malonylpolymethylenes[*1]

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Treatment of acetic anhydride with aliphatic dibasic acid chloride in the presence of 3 equivalents of aluminum chloride in nitrobenzene at 50°C afforded a polymer with the structure assigned to poly-malonylpolymethylene, $R\text{–}[(CH_2)_m\text{–}COCH_2CO]_n\text{–}(CH_2)_m\text{–}R$, ($R=\text{–}COOH$ and/or $\text{–}COCH_3$, $n=8\text{—}16$). Polymalonyl-heptamethylene, -hexamethylene and -pentamethylene were prepared and their properties were recorded. The product obtained by the reaction of acetic anhydride with adipoyl chloride seems to have a few cross-linkings in its structure.

In a previous report1) it was suggested that poly-malonylphenylene could be synthesized by the reaction of ethyl acetoacetate with terephthaloyl chloride in the presence of aluminum chloride according to the following reaction:

$$CH_3COCH_2COOC_2H_5 + C_6H_5COCl \xrightarrow[-CH_3COCl \atop -CO_2,\ -C_2H_5Cl]{AlCl_3} (C_6H_5CO)_2CH_2$$

However, a polymer was obtained which might be considered to be an aluminum chelate polymer consisting of phenylene and malonyl groups, some of which have a carbethoxy group. The polymer insoluble in ordinary organic solvents could not be freed from aluminum, and therefore was supposed to have three-dimensional structure containing some methine carbon atoms as in tribenzoylmethane, a minor product in the above reaction.

This paper deals with the synthesis of poly-malonylpolymethylene with a linear structure. In order to exclude reactions favorable for cross-linking formation as much as possible, several comparative and preliminary experiments using azelaoyl chloride in the presence of aluminum chloride were carried out with ethyl acetoacetate, acetyl chloride or acetic anhydride. The product was separated into a benzene-soluble and a benzene-insoluble fraction, from which an acetone-insoluble substance (if present) was removed, then the molecular weights of the fractions were determined. The reaction conditions and results are summarized in Table 1.

Treatment of ethyl acetoacetate with an equimolar quantity of azelaoyl chloride in the presence of aluminum chloride in nitrobenzene gave only a benzene-soluble product of low molecular weight at 50°C. Use of acetyl chloride in place of ethyl acetoacetate afforded a benzene-insoluble product contaminated with an acetone-insoluble substance, which increased with incease of acetyl chloride. In the case of acetic anhydride the benzene-insoluble product of relatively high molecular weight, obtained in a slightly lower yield, increased slightly with the increase of aluminum chloride. When the amount of azelaoyl chloride increased from 0.2 to 1 molar excess, an acetone-insoluble substance was formed and obtained as a single product in a high yield. The acetone-insoluble substance, from which aluminum could not be removed by the usual procedure, seems to have a three-dimensional structure owing to the acylation caused by the excess of acid chloride. For preparation of the required linear polymer, use of acetic anhydride is found to be most suitable.

Other than polymalonylheptamethylene, polymalonyl-hexamethylene and -pentamethylene were also prepared in a similar manner from acetic anhydride using suberoyl and pimeloyl chloride, respectively. Treatment with adipoyl chloride gave a benzene-insoluble product containing a small amount of an acetone-insoluble substance. The details and properties of the polymers are given in Table 2.

From the fact that dibenzoylmethane is obtained by the reaction2) of acetic anhydride or acetyl chloride with benzoyl chloride under a similar reaction condition, it seems that the polymer consists of malonyl and polymethylene groups. This is also supported by the formation of either its alkali salt insoluble in water only in the case of a polymer of higher molecular weight, or its copper complex (*e.g.*, copper content of the polymalonyl-

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1) K. Matsui, M. Motoi, T. Nojiri and K. Wakabayashi, This Bulletin, **41**, 1151 (1968).

2) T. Nojiri, H. Kataoka, O. Murata, T. Murai and K. Matsui presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

TABLE 1. REACTIONS OF ETHYL ACETOACETATE, ACETYL CHLORIDE, AND ACETIC ANHYDRIDE WITH AZELAOYL CHLORIDE

Reactant: $ClOC(CH_2)_7COCl$ 2.3 g (0.01 mol), a) 2.7 g (0.012 mol); b) 4.5 g (0.02 mol)
Solvent: Nitrobenzene 10 m*l*
Reaction temp: 50°C, c) 45°C

Substrate		AlCl₃ g	mole ratio	Reaction time day	Yield and mol. weight BS g	MW	BI g	MW
$CH_3COCH_2COOC_2H_5$	1.3 g (0.01 mol)	4.0	3	6	2.20	640		
CH_3COCl	0.8 g (0.01 mol)	2.7	2	2c)	0.62	450	1.04	1000
	1.6 g (0.02 mol)	2.7	2	6c)	0.67	540	1.35[*1]	2300
		4.0	3	6	0.77	610	1.36[*1]	2000
$(CH_3CO)_2O$	1.0 g (0.01 mol)	1.3	1	6	1.15	500	0.28	910
		2.7	2	2	1.98	700	—	
		2.7	2	5	1.64	800	0.36	3000
		4.0	3	6	1.16	600	0.68	2060
		a) 2.7	2	6	1.06	770	1.10[*1]	2100
		b) 2.7	2	6	—		2.3[*2]	

BS: Benzene-soluble polymalonylheptamethylene
BI: Benzene-insoluble polymalonylheptamethylene
MW: Molecular weight

[*1] This fraction was contaminated with an acetone-insoluble substance. The molecular weight was determined after removal of the contaminant.

[*2] An acetone-insoluble substance

TABLE 2. REACTION OF ACETIC ANHYDRIDE WITH DIBASIC ACID CHLORIDES

Substrate: $(CH_3CO)_2O$ 1.0 g (0.01 mol)
Condensing agent: $AlCl_3$ 4.0 g (0.03 mol)
Solvent: Nitrobenzene 10 m*l*
Reaction temp: 50°C
Reaction time: 6 days

Reactant (0.01 mol) $ClOC(CH_2)_mCOCl$ *m*	g		Yield, mol weight and property g	MW	State	Softening temp. °C
7	2.3	BS	1.16	600	brown paste	oily at 40
		BI	0.68	2060	brown flex. solid	50
6	2.2	BS	1.35	550	brown paste	oily at 40
		BI	0.29	1460	brown flex. solid	50
5	2.0	BS	1.03	450	brown paste	oily at 40
		BI	0.12	1450	dark brown rigid solid	80
4	1.9	BS	0.42	350	dark brown paste	oily at 40
		BI	0.13*	900	dark brown rigid solid	120

BS: Benzene-soluble polymer
BI: Benzene-insoluble polymer
MW: Molecular weight

* This fraction was contaminated with an acetone-insoluble substance. The molecular weight was determined after removal of the contaminant.

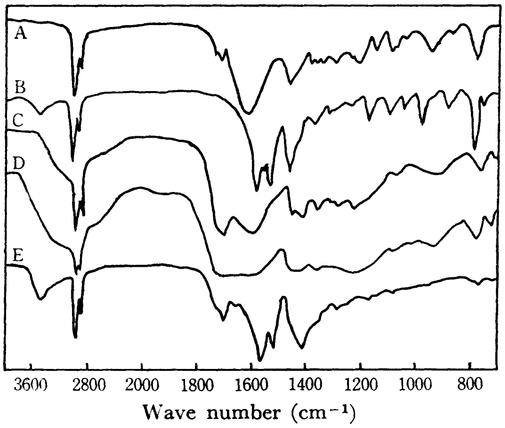

Fig. 1. Infrared spectrum of di-*n*-butyrylmethane (NaCl plate)(A); its copper chelate(KBr disk)(B); benzene-soluble polymalonylheptamethylene (NaCl plate)(C); benzene-insoluble polymalonylheptamethylene(NaCl plate)(D); and its copper chelate(KBr disk)(E).

heptamethylene complex was 11—15%; calculated for $Cu(C_8H_{15}C_2O_2)_2$: about 16%).

General aspects of the IR spectra of the benzene-soluble and -insoluble polymalonylheptamethylene resemble each other, except that absorptions at 1728 (sh), 1710 (m) and 1613 (br) cm^{-1} for the former are replaced by a broad band in the region 1742—1548 cm^{-1} for the latter. The spectrum of the former corresponds to that of di-*n*-butyrylmethane which exhibits absorptions at 1730 (w), 1708 (w) and 1616 (br) cm^{-1}. However, the spectrum of each polymer differs from that of di-*n*-butyrylmethane in having a broad band in 3500—3100 cm^{-1} region due to a hydroxy and a carboxyl group. The spectrum of the copper chelate of the benzene-insoluble polymer, though having the same absorption peaks at 1573 and 1522 cm^{-1} as those for the copper chelate of di-*n*-butyrylmethane, shows two additional absorptions. One is observed at 1710 cm^{-1}, which seems to be due to a carbonyl group not complexed with copper and to acetyl end group from the decarboxylation of β-ketonic acid group, and the other is a broad band centered at 3440 cm^{-1} attributed to hydroxy group, without an absorption due to carboxyl group. The NMR spectrum of the benzene-insoluble polymalonylheptamethylene shows two broad singlets at 6.40 τ ($COCH_2CO$), and 4.53 τ (vinyl proton on COCH=C(OH)), a sharp singlet at 7.95 τ ($COCH_3$ as end group). A similar spectral evidence was also observed generally from the IR and NMR spectra of the other polymers. On being burnt, all acetone-soluble polymers give ash, which is considered to be alumina derived from a small amount of the condensing agent (*e.g.*, less than 0.5% in the case of the benzene-insoluble polymalonylheptamethylene). However, no NMR signals were observed due to a methine group. Thus, the structure of the benzene-insoluble polymer can be assigned to poly-malonylpolymethylene:

$$R\text{-}[\text{-}(CH_2)_m-COCH_2CO\text{-}]_n\text{-}(CH_2)_m-R$$

$$R=-COOH \text{ and/or } -COCH_3;\ m=5,\ 6,\ 7;$$

$$n=8-16.$$

In the case of a polymer from adipoyl chloride which becomes easily dark brown in the presence of aluminum chloride, a small singlet at 7.14 τ attributed to a methine group appears even after removal of the acetone-insoluble substance. This suggests the presence of a few cross-linkings.

Experimental

Materials. Ethyl acetoacetate, acetyl chloride and acetic anhydride, commercial materials, were distilled and each stored in an ampul. Their bp were 75—77°C/15 mmHg, 52°C and 139°C, respectively. Commercial dibasic acids, azelaic, suberic and adipic acid, were converted into methyl esters, which were rectified *in vacuo* to give their glc charts showing sufficient purities, and were hydrolyzed to the original dibasic acids. Pimelic acid was prepared according to literature[3] and purified similarly. Acid chlorides of these acids were prepared by a modification of the methods in literature,[4] then rectified twice and stored separately in an ampul, bp 125—126°C/5 mmHg for azelaoyl chloride, by 126—127°C/6 mmHg suberoyl chloride, bp 106—107°C/4 mmHg pimeloyl chloride and bp 103—105°C/7 mmHg adipoyl chloride. Di-*n*-butyrylmethane was prepared according to literature,[5] bp 82—84°C/11 mmHg.

Measurements. The melting and softening points were determined on a Yanagimoto micro-melting point apparatus model MP-S 1 and uncorrected. The molecular weight was determined with a Hitachi model-115 vapor pressure osmometer in a 0.10—0.15/25 m*l* acetone solution at 35°C. The IR spectra (KBr for copper chelates, NaCl plate for polymers) were obtained on a Nihon Bunko model DS-301 infra-red spectrometer. The NMR spectra were measured on a Nihon Denshi-JEOL model C-60 H spectrometer operating at 60 MHz in 10—20 wt/vol% deuteriochloroform solutions with tetramethylsilane as internal standard.

Procedure. To a cold solution of aluminum chloride and substrate in dry nitrobenzene, which was placed a 50 m*l* flask equipped with a calcium chloride tube, dibasic acid chloride was added, and the mixture was kept in a thermostat at 50°C. The reddish brown gelatinous reaction mixture was stirred into a mixture of hydrochloric acid and crushed ice and then allowed to stand for 0.5 hr. The mixture was shaken with chloroform on a mechanical shaker for 1 hr. The

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3) J. M. Straley and A. C. Adams, "Organic Syntheses," Coll. Vol. II, p. 531 (1963).

4) C. H. Gerhart and L. Chiozza, *Ann. Chem.*, **87**, 293, (1853); D. Vorländer, *ibid.*, **280**, 183 (1884).

5) G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, **125**, 754 (1924).

organic layer separated was washed repeatedly by shaking with fresh 6 N hydrochloric acid for 15 min until the aqueous layer gave no detectable amount of aluminum compound, then was steam-distilled *in vacuo* to remove organic solvent. The residue dissolved in a small amount of chloroform was washed repeatedly with warm water to remove the dibasic acid and then was shaken with hot benzene to separate into a benzene-soluble and a benzene-insoluble fraction. The former, after partial evaporation, afforded an oil on addition of petroleum ether. From the latter an acetone-insoluble substance (if present) was separated by treatment with acetone followed by filtration. Evaporation of the filtrate gave an oil. Each oil obtained was dried *in vacuo* to a constant weight at 50°C.

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