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Hydrogen Transfer Polymerization of Malononitrile

Nariyoshi KAWABATA,* Chung Kuang CHEN, and Shinzo YAMASHITA
Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto
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Treatment of malononitrile with a catalytic amount of cuprous chloride and triethylamine under a nitrogen atmosphere resulted in the formation of solid polymer in high yield. The polymer was soluble in dimethyl sulfoxide, pyridine and hexamethylphosphoramide but insoluble in other organic solvents. The polymer was characterized by elemental analyses and IR and NMR spectra to have a mixed structure of an enamine form, $-[C(CN)=C(NH_2)]-_n$, and a ketimine form, $-[CH(CN)-C(=NH)]-_n$.

Only a few publications are available on the polymerization of malononitrile. Korshak *et al.*[1] made an attempt to polymerize malononitrile by the polyrecombination mechanism, *i.e.*,

$$CH_2(CN)_2 \xrightarrow{\cdot R} \left\{\begin{matrix} CN \\ | \\ C \\ | \\ CN \end{matrix}\right\}_n \quad (1)$$

but found the participation of nitrile group in the polymerization reaction.

$$CH_2(CN)_2 \xrightarrow{\cdot R} \left\{\begin{matrix} C=N \\ | \\ CH_2CN \end{matrix}\right\}_n \quad (2)$$

Whang *et al.*[2] followed up this reaction but obtained oily material from malononitrile. Jones[3] studied on the base-catalyzed polycondensation of mono- and dinitriles involving the reaction,

$$RCN \xrightarrow[\text{base}]{} \left\{\begin{matrix} C=N \\ | \\ R \end{matrix}\right\}_n \quad (3)$$

and obtained black, hard, and insoluble solid from malononitrile.

The authors have found the polymerization of malononitrile by the hydrogen transfer mechanism in the presence of cuprous chloride and triethylamine under a nitrogen atmosphere.

$$CH_2(CN)_2 \xrightarrow[\text{under } N_2]{Cu_2Cl_2,\ Et_3N} \left\{\begin{matrix} C=C \\ | \quad | \\ CN\ NH_2 \end{matrix}\right\}_n - \left\{\begin{matrix} CH-C \\ | \quad \| \\ CN\ NH \end{matrix}\right\}_{n'} \quad (4)$$

The mechanism of this polymerization might be related to the Thorpe reaction, *i.e.*, base-catalyzed condensation of nitrile.

$$RCH_2CN + R'CH_2CN \xrightarrow[\text{base}]{} R-\underset{\underset{CN}{|}}{CH}-\underset{\underset{NH}{\|}}{C}-CH_2R' \quad (5)$$

The Thorpe reaction gives mainly the dimer, β-iminonitrile, but in some cases trimer and its cyclized products. Condensation of malononitrile by the Thorpe reaction is also reported to give dimer, trimer, and cyclized trimers.[4] There appears to be, however, no report of the condensation of malononitrile to afford tetramer, higher oligomer nor polymer of the above type.

Experimental

Elemental analyses were performed at the Elemental Analyses Center of Kyoto University. IR spectra were recorded on a Japan Spectroscopic Co. Model 402G spectrometer. NMR spectra were obtained with a Japan Electron Optics Lab. Model 4H-100 spectrometer using tetramethylsilane as the external standard.

Materials. Malononitrile and triethylamine were puri-

* To whom inquiries should be directed.

1) S. L. Socin, V. V. Korshak, V. A. Vasnev, and E. L. Baranov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1962**, 1644.

2) J. J. Whang, E. J. Sinke, and R. K. Graham, *Amer. Chem. Soc., Div. Polymer Chem., Preprints*, **5**, 312 (1964).

3) I. B. Jones, *ibid.*, **5**, 239 (1964).

4) a) R. Schenk and H. Finken, *Ann. Chem.*, **462**, 267 (1928); b) D. M. W. Anderson, F. Bell, and J. L. Duncan, *J. Chem. Soc.*, **1961**, 4705; c) H. Junek and H. Sterk, *Z. Naturforsh.*, B **22**, 732 (1967), and, references therein.

fied by distillation. Guaranteed reagent of cuprous chloride was used without further purification. Nitrogen was purified by passing through a tube containing copper turnings in a furnace at 170°C followed by drying with silica gel and molecular sieves. Solvents were purified by the usual methods.[5] Other chemicals were commercially available and used without further purification.

Procedure. Polymerizations were carried out under a nitrogen atmosphere in pyrex test tubes with magnetic stirring. The polymer was recovered by pouring into a large excess of water, and was purified by reprecipitation from dimethyl sulfoxide - water system followed by drying under high vacuum over phosphorus pentoxide for prolonged periods. Viscosity measurements of polymer solutions were made in dimethyl sulfoxide at 30°C with a Ubbelohde-type dilution viscometer. Number average molecular weight of polymers was determined by ebullioscopy in pyridine using a Cottrell-type ebulliometer.

Results and Discussion

Malononitrile polymerizes easily in the presence of catalytic amount of cuprous salt and tertiary amine. For example, when 3.2 m*l* (50 mmol) of malononitrile was heated in 5.0 m*l* of tetrahydrofuran at 60°C in the presence of 1 mol% of cuprous chloride and 4 mol% of triethylamine under a nitrogen atmosphere for 19.5 hr, polymer was obtained in 91% yield. The polymer became a nearly colorless (slightly brown) powder after purification. Melting point of the polymer was higher than 300°C. The polymer was soluble in dimethyl sulfoxide, pyridine, and hexamethylphosphoramide, but insoluble in other organic solvents and water. The intrinsic viscosity of the polymer determined in dimethyl sulfoxide at 30°C was 0.044 d*l*/g. The number average molecular weight of the polymer determined in pyridine was about 1700,[6] *i.e.*, the degree of polymerization was about 26. Many experiments were carried out in order to increase both molecular weight and yield of the resulting polymer. Some of good results are given in Table 1. No catalyst more suitable than cuprous salt - tertiary amine system could be found for this polymerization reaction. Nitrogen atmosphere is desirable because the cuprous salt - tertiary amine system is a catalyst for air oxidation of organic compounds.

Table 1. POLYMERIZATION OF MALONONITRILE[a]

Solvent	(m*l*)	Et_3N/Cu_2Cl_2 mol ratio	Temp. (°C)	Time (hr)	Conv. (%)	$[\eta]$[b] (d*l*/g)
Dimethyl sulfoxide	4.5	2	50	43	82	0.043
Dimethyl sulfoxide	4.1	8	50	68	80	0.044
Dimethyl sulfoxide	4.0	4	50	43	82	0.041
Nitrobenzene	5.0	4	50	21	88	0.041
Tetrahydrofuran	5.0	4	60	19.5	91	0.044

a) Malononitrile, 3.2 m*l* (50 mmol); cuprous chloride, 0.1 g (1 mol% for the monomer); polymerizations were carried out under a nitrogen atmosphere.
b) Viscosity of polymalononitrile was measured at 30°C in dimethyl sulfoxide.

Elemental analyses of the polymer gave the following results; Found: C, 54.41, 54.88; H, 3.19, 2.91; N, 41.29, 41.23%. Calcd for $(C_3H_2N_2)_n$: C, 54.54; H, 3.05; N, 42.41%. These results indicate that the polymer has the same empirical formula as the monomer, *i.e.*, there would be no possibility of dehydrogenation nor hydrolysis during the polymerization.[7]

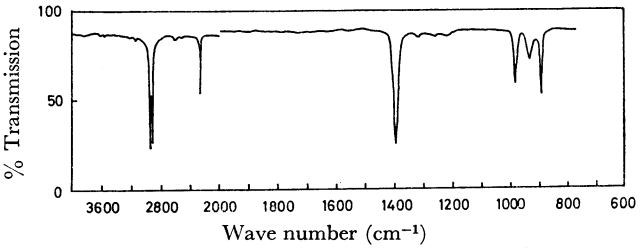


Fig. 1. IR spectrum of malononitrile monomer.

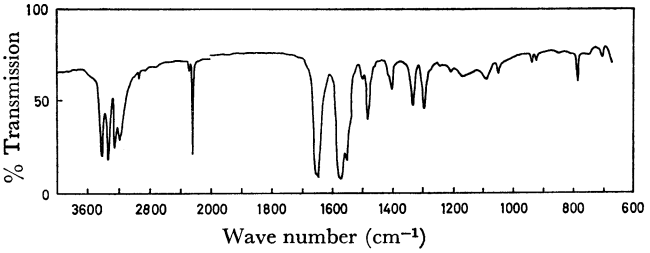


Fig. 2. IR spectrum of polymalononitrile in a KBr disk.

The IR spectrum of malononitrile monomer and that of the polymer in a KBr disk are shown in Figs. 1 and 2, respectively. The absorptions due to the methylene group of malononitrile monomer at 2938 and 2967 cm^{-1} disappeared during the polymerization. Absorptions between 3100—3500 cm^{-1} of the polymer are due to NH and/or NH_2 stretching vibrations, because the polymer has no oxygen as was pointed out by elemental analyses. The appearance of NH and/or NH_2 group together with the disappearance of the methylene group during the polymerization indicates the hydrogen transfer mechanism of the reaction. The authors concluded that the polymer has a mixed structure of an enamine form (I) and a ketimine form (II).

I II

As will be discussed later, IR and NMR spectra of the polymer are consistent with this conclusion. The absorptions at 3323 and 3399 cm^{-1} can be assigned to the NH_2 group of structure I, and those at 3167 and 3239 cm^{-1} to the NH group of structure II.[8] The absorptions of NH stretching vibration of ketimines are

5) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York (1970).
6) Two experiments gave 1500 and 1900 as the number average molecular weight of the polymer.
7) The observed nitrogen content of the polymer is somewhat lower than the calculated value. However, this result is probably due to slightly difficult combustion of the polymer.
8) The reason of this splitting into two absorptions will be discussed later.

reported to appear in the range of 3205—3236 cm^{-1}.[9] The weak absorption at 2919 cm^{-1} can be assigned to the stretching vibration of methine group of II. The absorptions at 2219 and 2267 cm^{-1} can be attributed to nitrile groups of I and II, respectively. The absorption at 1647 cm^{-1} may be due to C=C group of I and C=N group of II. The absorption at 1573 cm^{-1} may be ascribable to deformation vibration of NH and NH_2 groups.

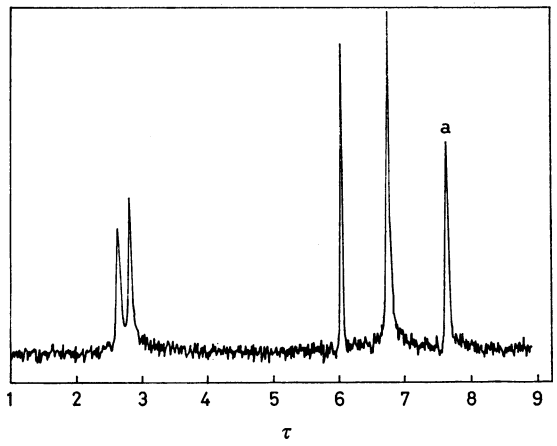


Fig. 3. Proton magnetic resonance spectrum of 5 wt % solution of polymalononitrile in dimethyl-d_6 sulfoxide. a: CH_3SOCH_3.

The NMR spectrum of the polymer obtained in dimethyl-d_6 sulfoxide is shown in Fig. 3. The peak at 6.04 τ can be assigned to NH_2 protons of structure I. The intensity of the peak at 6.75 τ is nearly equal to the total intensity of the two peaks at 2.63 and 2.82 τ. The former can be ascribable to CH proton and the latter two peaks to NH proton of structure II, respectively. Few data are available for NMR spectra of ketimines, but is reported to appear at 0.6 τ in the case of diphenylketimine.[10] The splitting of IR absorption of NH stretching vibration and that of NMR peak assigned to NH proton of structure II suggest that there are two types of imino groups in the polymer. Molecular model suggests the possibility of two types of steric circumstances around imino group, *i.e.*, *pseudo-isotactic* structure III and *pseudo-syndiotactic* structure IV with respect to the imino group, which are illustrated in Fig. 4.

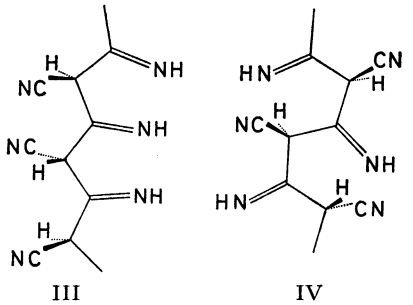
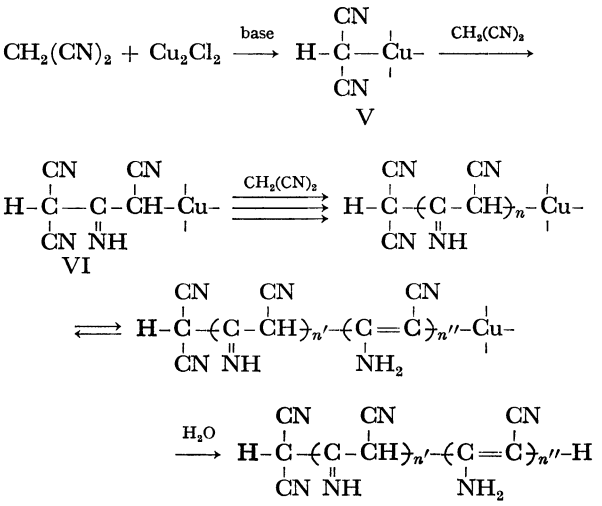


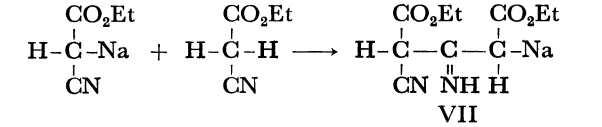
Fig. 4. Two types of possible steric circumstances around imino group of polymalononitrile.

The intensity ratio of the NMR absorption at 6.04 τ to that at 6.75 τ was 1 : 2.3. The ratio was not sensitive to change of concentration in the range of 1—10%. This result shows that in dimethyl sulfoxide solution, about 20% of monomer units have the enamine structure and the residual 80% the ketimine structure. This result consists with the general observation that the ketimine structure is more stable in the ketimine - enamine tautomerism.

Though the authors have no evidence concerning the mechanism of this polymerization, it would be reasonable to speculate as follows;



The formation of an organocopper compound V is conceivable, since the reaction of 1-hexyne with cuprous chloride and ammonia is reported to give 1-hexynylcopper.[11] The formation of VI by the reaction of V with malononitrile is also conceivable, because diethyl β-imino-α-cyano-α'-sodioglutarate VII is reported to be obtained by the following reaction.[12]



9) P. L. Pickard and G. W. Polly, *J. Amer. Chem. Soc.*, **76**, 5169 (1954).
10) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *ibid.*, **87**, 5085 (1965).
11) W. J. Gensler and A. P. Mahadevan, *J. Org. Chem.*, **21** 180 (1956).
12) H. Baron, F. G. P. Remfry, and J. F. Thorpe, *J. Chem. Soc.*, **85**, 1726 (1904).