

Synthesis of Alternating Copolymalonamides by Ring-Opening Polyaddition Reaction of Bismalonimide with Diamines

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ABSTRACT: A new *N,N'*-disubstituted bismalonimide was synthesized by the cycloaddition of methylenebis(4-phenylisocyanate) with pentamethyleneketene. Ring-opening polyaddition reaction of the bismalonimide with aliphatic diamines was carried out in *N*-methyl-2-pyrrolidone to give a new class of alternating copolymalonamides having inherent viscosity of 0.5-1.0 in quantitative yield. The solution polymerization was almost completed at room temperature within 24 hr, or at 80°C within an hour. In methyl ethyl ketone, precipitation of polymer occurred to yield the polymer with rather lower inherent viscosity. The alternating copolymalonamides were amorphous, and showed melt temperature in the range of 150-200°C.

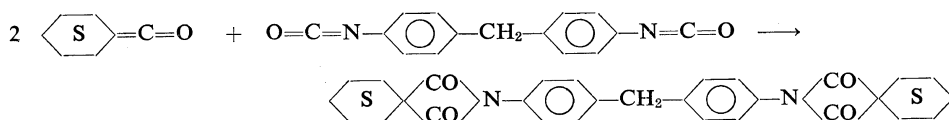
KEY WORDS Alternating Copolymalonamides / Ring-opening Polyaddition Reaction / Bismalonimide / Diamines / *N*-Methyl-2-pyrrolidone / Infrared Spectra / Solubility / X-Ray Diffraction Diagrams / Thermal Behavior /

Ring-opening polyaddition reaction of *N,N'*-disubstituted bisimides with diamines has recently received considerable attention in the preparation of ordered copolyamides. Typical examples are the regularly alternating mixed polysuccinamides and polyglutaramides obtained from the corresponding five-membered and six-membered bisimides, respectively, by both melt¹⁻³ and solution² polymerization techniques. In the present paper the synthesis is described of a new and more reactive four-membered bisimide, which is subjected to the ring-opening polyaddition reaction with diamines to form high-molecular-weight alternating copolymalonamides under mild ambient conditions.

RESULTS AND DISCUSSION

Synthesis of Bismalonimide

Although several methods are known for the preparation of monomalonimides,⁴ the only bismalonimide described in the literature was obtained by a ring-closure method.⁵ In this paper the successful synthesis discussed of *N,N'*-methylenediphenylenebis(2,2-pentamethylenemalonimide) (BMI) by the cycloaddition reaction of methylenebis(4-phenyl isocyanate) (MDI) and pentamethyleneketene in refluxing toluene by modifying the method described by Poshkus and Herweh.⁶ The yield of purified BMI was 25%. During the course of this investigation, it was reported independently by Martin, *et al.*,⁷ that several bismalonimides were prepared by a method similar to the one mentioned here.



BMI showed infrared (IR) absorption bands at 1855 cm⁻¹ and 1730 cm⁻¹ characteristic of a four-

membered imide ring⁵, as given in Figure 1. Elemental analysis of BMI was also in close

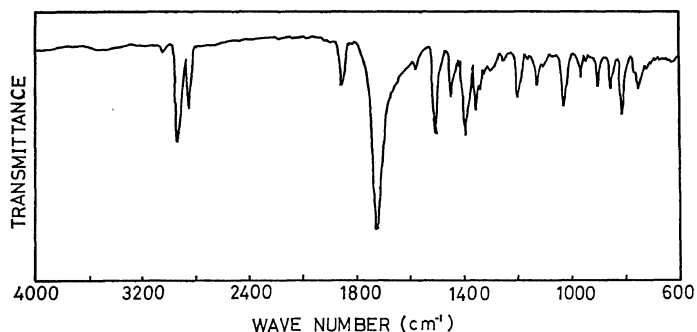


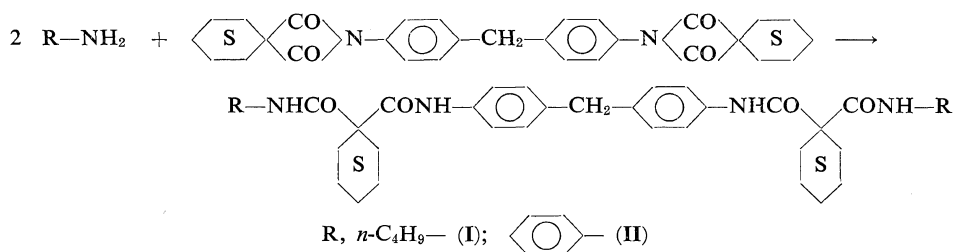
Figure 1. Infrared spectrum of the monomer BMI on a KBr pellet.

agreement with the expected structure.

of BMI was attempted with typical aliphatic and aromatic amines.

Model Reaction

Prior to polymer synthesis, the model reaction



n-Butylamine reacted readily with BMI in 78-% yield in tetrahydrofuran (THF) at room temperature to give the ring-opening adduct I,

which was identified by elemental analysis. IR spectrum of the adduct I is shown in Figure 2. On the other hand, aniline was less reactive

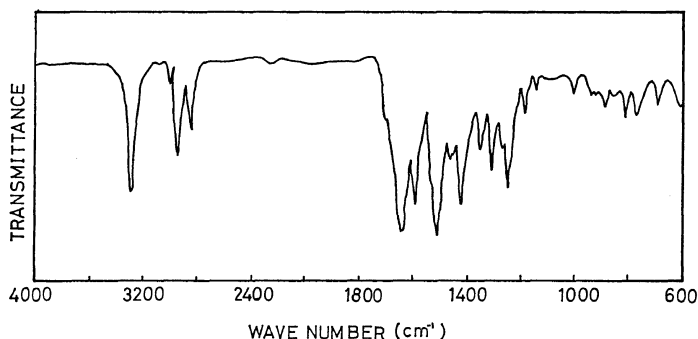


Figure 2. Infrared spectrum of the ring-opening adduct I on a KBr pellet.

than *n*-butylamine toward BMI, and the reaction required an elevated temperature. The reaction in *N*-methyl-2-pyrrolidone (NMP) at 150°C yielded a trace amount of the adduct II, which was determined by elemental analysis, and that in

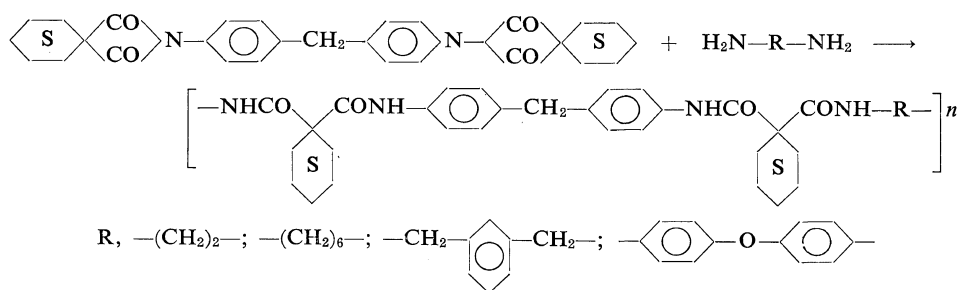
refluxing toluene in the presence of *p*-toluenesulfonic acid gave the product II in 11-% yield. IR spectrum of the adduct II was essentially identical with that of the adduct I.

Synthesis of Alternating Copolyamides

Ring-opening Polyaddition Reaction

The ring-opening polyaddition reaction of BMI

with aliphatic and aromatic diamines proceeded according to the following equation.



The polymerization was carried out in NMP and methyl ethyl ketone (MEK) at ambient and elevated temperatures. The results are listed in

Table I. Ring-opening polyaddition reaction of BMI with various diamines in NMP^a

Diamine	Reaction condition		Polymer	
	Temp, °C	Time, hr	Yield, %	η_{inh}^b
$-(\text{CH}_2)_2-$	10—20	24	94	0.50
$-(\text{CH}_2)_6-$	10—20	24	99	0.89
$-\text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2-$	10—20	24	99	0.81
$-\text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 -$	70—80	24	24	0.09

^a Monomer concentration was 0.0025 mol of the reactants in 5 ml of NMP.

^b Measured at a concentration of 0.5 g/dl in concentrated sulfuric acid at 30°C.

Tables I and II.

Figures 3 and 4 show the rate of polymerization of BMI with hexamethylenediamine (HMDA) in NMP in terms of solution viscosity of polymers. The reaction proceeded fairly slowly in solution at room temperature and was

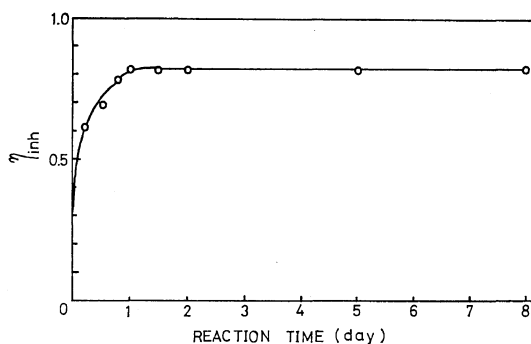


Figure 3. Polymerization of BMI with HMDA in NMP at room temperature.

Table II. Ring-opening polyaddition reaction of BMI with hexamethylenediamine under various reaction conditions

Solvent ^a	Additive, ^b g	Reaction condition		Polymer	
		Temp, °C	Time, hr	Yield, %	η_{inh}^c
NMP	None	10—20	24	99	0.89
"	None	70—80	24	99	0.82
"	Water, 0.01	10—20	24	96	0.63
"	TED, 0.03	10—20	24	99	0.80
MEK	None	70—80	6	99	0.33
"	Water, 0.01	70—80	6	99	0.36
"	Water, 1.0	70—80	6	99	0.48
"	TED, 0.03	70—80	6	97	0.30

^a Monomer concentration was 0.0025 mol of the reactants in 5 ml of NMP or in 10 ml of MEK.

^b TED denotes triethylenediamine.

^c Measured at a concentration of 0.5 g/dl in concentrated sulfuric acid at 30°C.

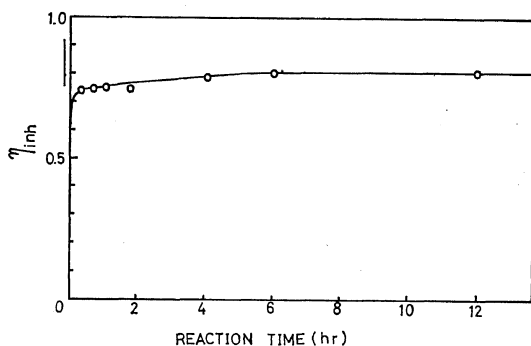


Figure 4. Polymerization of BMI with HMDA in NMP at 80°C.

almost completed within a day to form the alternating copolyamalonamide having a high molecular weight, whereas the reaction at 80°C reached essential completion within an hour. The reaction temperature had no effect on the attained molecular weight of the polymer.

As shown in Table I, the reaction of BMI with aliphatic diamines such as ethylenediamine, hexamethylenediamine, and *m*-xylylenediamine, quite readily gave alternating copolyamalonamides having a high inherent viscosity in the range of 0.5–1.0. However, the reaction with bis(4-aminophenyl)ether took place much more slowly than that of aliphatic diamines as can be anticipated from the result of the model reaction. Neither the yield nor the molecular weight of the copolyamalonamide was satisfactory.

The polymerization was greatly influenced by the solvent (Table II). The reaction in NMP proceeded in a homogeneous phase to give a high-molecular-weight polymer, as discussed

above. However, use of MEK as a solvent reduced the inherent viscosity to almost one half, although the yield of the polymer was nearly quantitative. The reason may be ascribed to the heterogeneous reaction phase, since copolyamalonamide was gradually precipitated out of the solution in MEK during the course of the polymerization.

The addition of water to the reaction medium, particularly to MEK, seemed to be effective for increasing the molecular weight of the polymer to some extent. The positive effect of the binary system of MEK and water has been found previously in the preparation of a high-molecular-weight polyamide-acid.⁸ Triethylenediamine as a catalyst was ineffective in this ring-opening polyaddition reaction.

Properties of Alternating Copolyamalonamides

Polymers obtained here were identified as polyamides from their infrared spectra and elemental analyses. IR spectrum of the typical polymer is given in Figure 5. The characteristic absorption bands of malonimide at 1855 cm^{-1} and 1730 cm^{-1} disappeared, while the spectrum showed the characteristic of secondary amide at 3340, 1650, 1520, and 1310 cm^{-1} . The spectrum of the polymer was very similar to that of the ring-opening adduct shown in Figure 2.

These alternating copolyamalonamides were soluble in *N,N*-dimethylacetamide, NMP, *m*-cresol, and concentrated sulfuric acid, and were partially soluble or swollen in formic acid and pyridine. They were insoluble in common organic solvents. Transparent and tough films were obtained by casting from dimethylacetamide

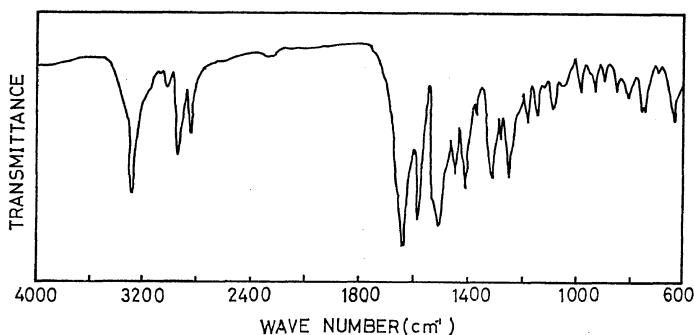


Figure 5. Infrared spectrum of a film of the polymer obtained from BMI and HMDA.

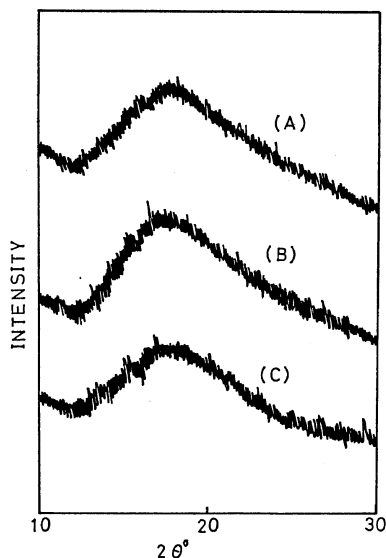


Figure 6. X-Ray diffraction diagrams of the polymers obtained from various diamines and BMI: (A) from HMDA; (B) from *m*-xylylenediamine; (C) from ethylenediamine.

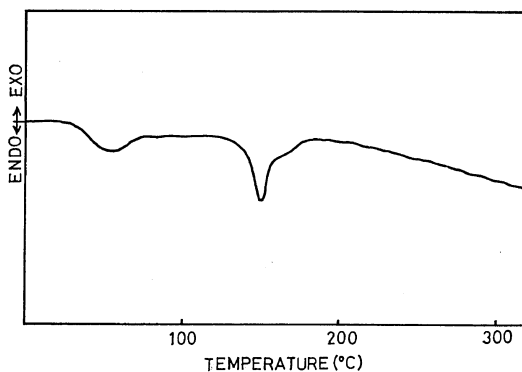


Figure 7. DTA curve of the polymer obtained from BMI and HMDA in N_2 at a heating rate of $15^\circ C/min$.

solution.

X-Ray diffraction diagrams of films of the polymers, shown in Figure 6, were obtained by the use of nickel-filtered $CuK\alpha$ radiation. The diagrams indicate that the alternating copolymalonamides were all amorphous.

Melting points and decomposition temperatures of the polymers were determined by means of differential thermal analysis (DTA) and thermo-

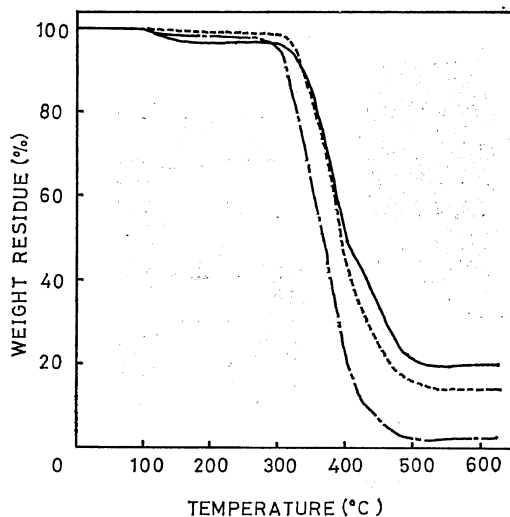



Figure 8. TGA curves of the polymers obtained from various diamines and BMI in N_2 at a heating rate of $5^\circ C/min$: ---, from HMDA; —, from ethylenediamine; ----, from *m*-xylylenediamine.

Table III. Thermal behavior data of alternating copolymalonamides from BMI and diamines

Diamine	PMT, ^a °C	Decomposition temperature, ^b °C
$-(CH_2)_2-$	175	335
$-(CH_2)_6-$	150	310
$-CH_2-$  $-CH_2-$	185	330

^a Polymer-melt temperature determined by DTA in N_2 (heating rate, $15^\circ C/min$).

^b Decomposition temperature observed by TGA in N_2 (heating rate, $5^\circ C/min$). The temperature given is that at which weight loss of a polymer reaches a value of 10% based on the original weight.

gravimetric analysis (TGA), respectively. The curves are given in Figures 7 and 8, and the thermal behavior data are summarized in Table III. The alternating copolymalonamides obtained here show polymer-melt temperature in the range of 150 – $200^\circ C$, and a breakdown at a temperature above $300^\circ C$ in a nitrogen atmosphere.

The low polymer-melt temperature is presumed to be lack of hydrogen bonding between amide

linkages by steric hindrance of bulky cyclohexane rings along the polymer chain.

EXPERIMENTAL

Materials

Cyclohexanecarboxylic acid, *n*-butylamine, aniline, ethylenediamine, and hexamethylenediamine, were all reagent-grade materials, and were used without any particular purification. Methylenebis(4-phenyl isocyanate) (provided by Nippon Polyurethane Industries Co.) and *m*-xylylenediamine (provided by Showa Denko Co.) were distilled under reduced pressure before use. Bis(4-aminophenyl) ether, provided by Sumitomo Chemical Co., was purified by recrystallization from tetrahydrofuran. Toluene, tetrahydrofuran, and methyl ethyl ketone (MEK) were obtained commercially in reagent grade and were used without any treatment except storage over molecular sieves 4A. *N*-methyl-2-pyrrolidone (NMP, provided by Mitsubishi Chemical Industries Ltd.) was purified by vacuum distillation and stored over molecular sieves 4A. Other materials were all obtained commercially.

Synthesis of Bismalonimide

Cyclohexanecarbonyl chloride was prepared in 84% yield by a conventional method from the corresponding carboxylic acid and excess of thionyl chloride, bp 78°C (22 mm) [lit.⁹ bp 67°C (14 mm)].

Bismalonimide was synthesized principally by the extension of the method described by Poshkus and Herweh,⁶ by the cycloaddition reaction of pentamethyleneketene derived from cyclohexanecarbonyl chloride and methylenebis(4-phenyl isocyanate). Typical synthesis is shown below.

Into a stirred solution of 30 g (0.2 mol) of cyclohexanecarbonyl chloride in 100 ml of toluene, 25 g (0.24 mol) of triethylamine was added within 20 min at room temperature. After stirring for 1 hr, the reaction mixture was then filtered. The filter cake was identified as triethylamine hydrochloride. The filtrate containing mainly pentamethyleneketene was added to a solution of 15 g (0.06 mol) of methylenebis(4-phenyl isocyanate) in 100 ml of toluene. The mixture was refluxed for 48 hr with stirring. The cooled, turbid reaction mixture was again filtered, and the second filter cake was also identified as

triethylamine hydrochloride. The filtrate was evaporated followed by washing the residue with cyclohexane. Repeated recrystallization from ethanol gave white leaflets melting at 203.5–204°C. The yield of pure *N,N'*-methylene-diphenylenebis(2, 2-pentamethylenemalonimide) (BMI) was 7.2 g (25% based on the diisocyanate).

Anal. Calcd for $C_{29}H_{30}N_2O_4$:

C, 74.01; H, 6.44; N, 5.95.

Found: C, 74.53; H, 6.63; N, 5.80.

Model Reaction of BMI with *n*-Butylamine

A solution of 1.18 g (0.0025 mol) of BMI and 0.37 g (0.005 mol) of *n*-butylamine in 12 ml of tetrahydrofuran was stirred at room temperature for 12 hr. The white precipitate formed was collected by filtration, washed with the fresh solvent, and dried. The ring-opening adduct I, melting at 223–224°C, weighed 1.21 g (78%).

Anal. Calcd for $C_{37}H_{52}N_4O_4$:

C, 72.02; H, 8.51; N, 9.08.

Found: C, 73.19; H, 8.59; N, 9.04.

Model Reaction of BMI with Aniline

A solution of 2.35 g (0.005 mol) of BMI, 1.02 g (0.011 mol) of aniline, and 0.02 g of *p*-toluenesulfonic acid in 10 ml of toluene was refluxed for 20 hr with stirring. The white solid precipitated was filtered, and recrystallized from benzene. The ring-opening adduct II was obtained as white needles and melted at 274°C. The yield of the pure product was 0.38 g (11%).

Anal. Calcd for $C_{41}H_{44}N_4O_4$:

C, 74.96; H, 6.77; N, 8.53.

Found: C, 73.82; H, 6.33; N, 8.65.

Solution Polymerization in NMP

Two typical examples of polymerization procedure are as follows.

A solution of 1.18 g (0.0025 mol) of BMI and 0.29 g (0.0025 mol) of hexamethylenediamine in 5 ml of NMP was reacted with stirring at room temperature for 24 hr. The slightly viscous solution formed was poured into 200 ml of acetone. The resulting polymer was filtered, followed by washing with boiling acetone, and drying at 60°C under vacuum. The yield was 1.46 g (99%). Inherent viscosity of the polymer in concentrated sulfuric acid was 0.89, measured at a concentration of 0.5 g/dl at 30°C.

Synthesis of Alternating Copolymalonamides

Anal. Calcd for $(C_{35}H_{40}N_4O_4)_n$:

C, 72.38; H, 6.96; N, 9.65.

Found: C, 70.92; H, 8.30; N, 9.44.

In a similar manner as above, BMI and *m*-xylylenediamine as diamine component gave the polymer having inherent viscosity of 0.81 in quantitative yield.

Anal. Calcd for $(C_{37}H_{42}N_4O_4)_n$:

C, 73.22; H, 6.99; N, 9.23.

Found: C, 72.51; H, 7.72; N, 9.20.

Solution Polymerization in MEK

A typical preparation is given below.

Into a hot solution of 1.18 g of BMI in 10ml of MEK was added 0.29 g of hexamethylenediamine all at once, and the resulting solution was refluxed at 70–80°C. The polymer was precipitated out of the solution as the reaction proceeded. After refluxing for 6 hr, the separated polymer was collected, washed with acetone, and dried at 60°C under vacuum. The yield was 1.46 g, and the inherent viscosity was 0.33.

Measurements

The infrared spectra were obtained on a Japan Spectroscopic Co. diffraction grating infrared spectrophotometer, Model IRA-1.

The X-ray diffraction diagrams were obtained in a Rigaku Denki X-ray diffractometer, Model RU-3H.

Thermal-behavior data were obtained by use of a Simazu micro-differential thermal analyzer, Model DT-20B, and its micro-thermogravimetric analyzer, Model TGC-20 and TG-20.

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