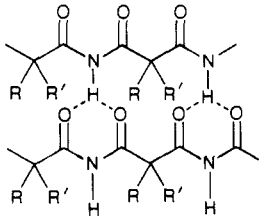
Communications to the Editor

Poly(3-butyl-3-ethylmalonimide) by Ring-Opening Polymerization

Introduction. Polymalonimides have not been described in the literature, even though interesting properties can be expected from these polymers, such as very efficient hydrogen bonding between the chains. Such bifurcated H bonds in imides have already been seen in X-ray crystal-structure determination.[1]



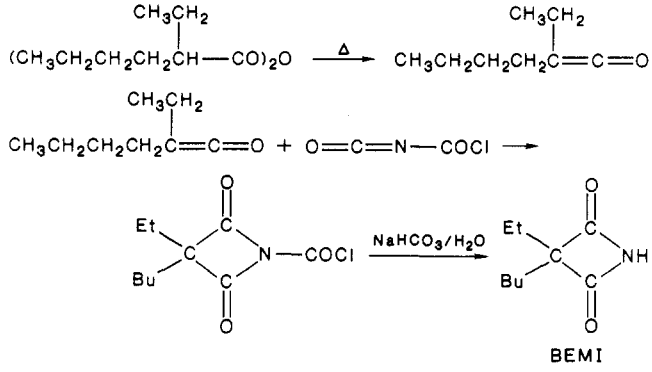
The method of choice to obtain these polymers should be ring-opening polymerization of the malonimide ring, a four-membered ring which is expected to be highly strained. For anionic or hydrolytic ring-opening polymerization, the monomer should be unsubstituted at nitrogen.

Staudinger, in the first reported synthesis of a malonimide, 3,3-diphenyl-*N*-phenylmalonimide, used the cycloaddition reaction between phenyl isocyanate and diphenyl ketene.[2] Swiss workers recently reported the synthesis of a malonimide unsubstituted at nitrogen, via a multistep and rather tedious reaction scheme, starting from ethyl cyanoacetate.[3] Overall yields were in the 3–5% range.

The cycloaddition route is much more practical and shorter, but the isocyanate must be carefully chosen. The isocyanate must be reactive in the cycloaddition with a ketene, and for this an electron-withdrawing substituent is needed on nitrogen. This group also must be easily removed after the cycloaddition. Chlorosulfonyl isocyanate (CSI) has been used successfully in the synthesis of N-substituted β-lactams.[4,5] By contrast, cycloaddition of CSI to ketene yields, after treatment with methanol, dimethyl malonate,[6] indicating that the highly strained malonimide ring decomposes under these conditions.

In order to obtain a malonimide derivative unsubstituted at nitrogen, we opted for the cycloaddition of another electron-poor isocyanate, chlorocarbonyl isocyanate, to a disubstituted ketene. After hydrolysis and decarbonylation, the malonimide derivative can be subjected to anionic ring-opening polymerization to yield the desired polymalonimide.

Results and Discussion. 3-Butyl-3-ethylmalonimide (BEMI) was synthesized via cycloaddition of butyl ethyl ketene[7] and chlorocarbonyl isocyanate. Butyl ethyl ketene is readily obtained from pyrolysis of 2-ethylhexanoic anhydride and is much more stable and easier to handle at room temperature than dimethyl ketene. Cycloaddition to chlorocarbonyl isocyanate occurs readily at room temperature in good yield. The hydrolysis and decarbonylation of the chlorocarbonyl substituent proceeded at room temperature under heterogeneous conditions in good yield. BEMI is stable at room temperature for short periods of time but can be kept at −45 °C indefinitely. The cycloaddition pathway to the malonimide derivatives is a much shorter and efficient method than the ring closure of malonic acid derivatives.



BEMI was polymerized by using anionic initiators. The results are summarized in Table I. The best results were obtained using potassium butoxide as initiator in bulk.

The obtained polymers were white solids, soluble in common organic solvents such as acetone and chloroform. The ^{13}C spectrum of the polymer is very similar to that of the monomer but several signals can be observed for the carbonyl carbon, indicating changes in tacticity. The inherent viscosities for runs 1 and 2 were too low to be determined, but run 4 yielded polymer with $\eta_{inh} = 0.37$ dL g^{-1}. No glass transition temperature for this last polymer could be observed by DSC; the melting point was 240 °C.

Conclusion. The anionic ring-opening polymerization of BEMI proceeds in mild conditions. This preliminary investigation of malonimides opens the way to a new class of monomers for ring-opening polymerization with a great potential for interesting properties.

Experimental Section. General Methods. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. NMR spectra were recorded using a 250-MHz WM-250 Varian spectrometer.

2-Ethylhexanoic acid and chlorocarbonyl isocyanate were obtained from Aldrich and used without further purification.

Butyl Ethyl Ketene. 2-Ethylhexanoic anhydride was prepared from 2-ethylhexanoic acid (288 g, 2 mol) and acetic anhydride (300 g, 3 mol). The reagents were stirred for 4 h at 120 °C, after which acetic acid and excess acetic anhydride were distilled out at aspirator pressure. 2-Ethylhexanoic anhydride was distilled at 101 °C (0.25 mmHg); yield, 92%.

Butyl ethyl ketene was prepared by pyrolysis of 2-ethylhexanoic anhydride. A quartz pyrolysis tube (50 cm × 25 mm), filled with quartz chips, was placed vertically in a tube furnace at 525 °C. The starting material was placed in an addition funnel and heated to about 100 °C. A large water-cooled receiving flask and a trap preceded a cold trap at −78 °C in which the ketene would be collected. The whole system was purged with Ar and the pressure was lowered to 2–3 mmHg. After the pressure and temperature are stabilized, 2-ethylhexanoic anhydride was dropped onto the column at a rate of 1–2 mL/min. Butyl ethyl ketene was collected in the cold trap as a yellow liquid and purified by a trap-to-trap distillation (28 °C (2–3 mmHg); yield, 33%).

3-Butyl-3-ethylmalonimide (BEMI). Chlorocarbonyl isocyanate (5 mL, 62 mmol) was dissolved in 30 mL of dry toluene under argon atmosphere and cooled with ice–water. Butyl ethyl ketene (7.8 g, 62 mmol) was added dropwise

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Table I
Polymerization of BEMI[a]

run	initiator (mol %)	cocatalyst (mol %)	solvent	yield, %	η_{inh}
1	NaH (6)	Ac_2O (3)	CH_3CN[b]	77	
2	NaH (6)	Ac_2O (3)	DMSO	38	
3	KH[c]	PhNCO (3)		100	0.07
4	KO-*t*-Bu (2.5)			58	0.37

[a] Under argon atmosphere at 28 °C for 20 h. [b] Heterogeneous. [c] Could not be weighed accurately.

and the reaction mixture was stirred for an additional 2 h. After the toluene had been evaporated, the residue was added to 60 mL of water, containing 5.2 g (62 mmol) of $NaHCO_3$. The heterogeneous reaction mixture was stirred overnight. The mixture was extracted with 25 mL of ether. After acidification of the aqueous layer with 2 N HCl, it was again extracted with 15 mL of ether. The ether extracts were combined, washed with water, dried over Na_2SO_4, and filtered and the ether was evaporated. The residue was distilled by using a short-path distillation head; bp 103–110 °C (0.7 mmHg). A clear colorless liquid was obtained; yield, 7.15 g (68%). The product was distilled a second time and the fraction between 92 and 95 °C (0.2 mmHg) was collected. Only one spot was obtained on TLC for this fraction (R_f = 0.76 in Et_2O; R_f = 0.63 in $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.905 (t, 3 H), 1.025 (t, 3 H), 1.36 (m, 4 H), 1.70 (m, 2 H), 1.760 (g, 2 H), 8.54 (br s, NH); ^{13}C NMR ($CDCl_3$) δ 8.81 (CH_3 of Bu), 13.51 (CH_3 of Et), 22.55, 23.42, 26.63 ($3CH_2$ of Bu), 29.75 (CH_2 of Et), 69.15 (C_{quart}), 173.78 (C=O); IR (KBr) 3574, 3245 (br, NH), 2962, 2935, 2876, 1736 (vs), 1460, 1383, 1347, 1274, 1158, 1096, 967 cm^{-1}; MS (EI probe) *m/e* 169 (M^+, 0.4%), 141 (–CO), 127 (–CON), 126 (26%, –CONH), 98 (60%), 83 (73%), 55 (100%, $CH_3CH_2C^+CH_2$ or $CH_3C^+{=}C{=}O$). Anal. Calcd: 63.88, C; 8.93, H; 8.28, N. Found: 63.81, C; 9.17, H; 8.18, N.

Polymerization Procedure. All polymerizations were run for 20 h at room temperature under argon atmosphere. The polymers were dissolved in chloroform, preciptated in ether, filtered, dried, and weighed. The inherent viscosities were determined in chloroform at 30 °C (concentration 50 mg/10 mL). Mp 240 °C (no tg); ^1H NMR ($CDCl_3$) 3 broad peaks, δ 2.1, 1.3, 0.9; ^{13}C NMR ($CDCl_3$) δ 9.57 (CH_3 of Bu), 13.68 (CH_3CH_2), 22.50, 32.20, 38.97 (CH_2 of Bu), 38.97 (CH_3CH_2), 61.19 (C_{quart}), 170.5, 171.0, 174.8, 175.8 (C=O); IR (KBr) 3200 (br), 2960, 1760, 1470, 1420, 1205, 1145, 965, 902, 780, 631 cm^{-1}. Anal. Calcd: 63.88, C; 8.93, H; 8.28, N. Found: 63.63, C; 8.88, H; 8.29, N.

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Electrooxidative Polymerization of Thiophenol To Yield Poly(*p*-phenylene sulfide)

There is currently a great interest in coating electrodes with thin polymer films by electrooxidative polymerization of aromatics such as pyrrole,[1] thiophene,[2] aniline,[3] phenol,[4] and benzene.[5] However, electrooxidative polymerization of thiophenol has not been reported; anodic oxidation of thiophenol merely yields diphenyl disulfide. Poly(*p*-phenylene sulfide) (PPS) is commercially produced by the polycondensation of *p*-dichlorobenzene and sodium sulfide at high pressure and temperature.[6] This paper describes the electrooxidative polymerization of thiophenol in the presence of an acid to yield pure PPS efficiently at room temperature. A polymerization mechanism is also described based on electrochemical measurement.

Thiophenol was dissolved in dry nitromethane containing 1.5 M trifluoroacetic acid and kept under dry atmosphere in a one-compartment cell with a pair of platinum plates as a working and an auxiliary electrode. The electrolysis was carried out with controlled potential at 2.0 V (vs Ag/AgCl). During the electrolysis the solution around the working electrode was colored brown and white polymer was precipitated. After the electrolysis (2 F/mol) the polymer was isolated by simple filtration in a 77% yield as white powder having an empirical formula $C_6H_4S_1$. Atomic absorption analysis with the sensitivity of 10^{-3}% of the polymer sample revealed no salts such as sodium chloride with which a commercial PPS is often contaminated. The structure including the 1,4-phenylene unit was confirmed by IR spectrum.[7] The polymer was soluble in hot *N*-methylpyrrolidone and its melting point at 180–190 °C suggested a molecular weight of more than 10^3.

The polymerization also proceeded in the presence of other acids such as sulfuric acid and stannic chloride, although the polymer yield and molecular weight were influenced by the added acid and solvent species. The polymerization was inhibited by basic solvents such as methanol and *N,N*-dimethylformamide and by water.

The cyclic voltammogram of thiophenol in the presence of trifluoroacetic acid was measured. The first oxidation peak was observed at 1.6 V, which has been attributed[8] to the oxidation of thiophenol to yield diphenyl disulfide. The second peak current was measured at 1.8 V, which has been attributed to the oxidation of diphenyl disulfide to its cation radical, the product of which has been allowed to react nucleophilically and irreversibly with basic species such as acetonitrile as in previous work.[8] In the strongly acidic atmosphere of this experiment, it is considered that this cationic species formed by the oxidation at 1.8 V leads to the PPS formation.

The reaction mixture had a brown color during the electrolysis, which disappeared by the addition of bases. This visible absorption is enhanced in the presence of the acid. From these results, the polymerization mechanism is illustrated in Scheme I: the cation which is produced by oxidation of diphenyl disulfide is assumed to be an

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