

Alternating Copolymers of Dimethylmaleic Anhydride

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Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

SUMMARY

Copolymerization of 2,3-dimethylmaleic anhydride was accomplished with vinyl ethers, particularly n-butylvinyl ether and isobutylvinyl ether and gave exactly alternating copolymers in all proportions of feed comonomer compositions. 2,3-Dimethylmaleic anhydride has not yet been copolymerized with vinyl comonomers with less electron donating properties.

INTRODUCTION

The alternating copolymerization of maleic anhydride (MA) with vinyl monomer has been extensively studied (WAGNER-JAUREGG, J., 1930). MA is a powerful electron accepting monomer and consequently copolymerizes readily with electron donating monomers although it does not homopolymerize under normal conditions. Only very recently has the polymerization to obtain linear poly-MA of reasonable molecular weight been accomplished (GAYLORD, N.G. and MAITY, S., 1973). A number of electron donating monomers have been used to prepare alternating copolymers of MA as, for example, ethylene (JOHNSON, J.H. and SCHAEFFGEN, J.R., 1963), 2-butene (TANAKA, T. and VOGL, O., 1974), dienes (STOYACHENKO, G.S. et.al., 1973), vinyl ethers (FIELD, N.D. and LORENZ, J.H., 1970), vinyl esters (CAZE, C. and LOUCHEUX, C., 1975), styrene (TSUCHIDA, E. and TOMOTO, T., 1971), and its substituted derivatives and stilbene (TANAKA, T. and VOGL, O., 1974).

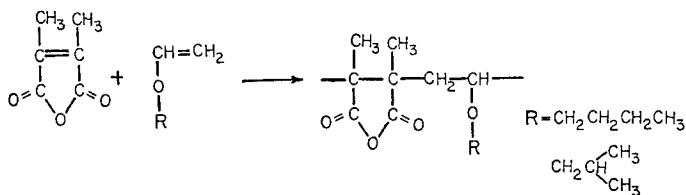
Very little work has been reported on the copolymerization of substituted maleic anhydride derivatives and other highly sterically hindered electron accepting monomers of the maleic and fumaric acid series. It was generally shown that some polymerizations involving such monomers proceeded extremely slowly and gave only low molecular weight polymers, with the polymers having an alternating structure (FUJIMORI, K. and BUTLER, G.B., 1972).

Low molecular weight copolymers of olefin monomers and substituted maleic anhydrides such as methyl maleic anhydride, dimethyl maleic anhydride, diethyl maleic anhydride and mono and dihalogen

substituted maleic anhydrides have been claimed in the patent literature (KUNTZ, I., 1975; TULLER, H.W. and NUSSBAUM, R.W., 1978; EVANI, S. and RAYMOND, R.J., 1979). Many of these copolymers have been claimed to exist in patents where the copolymerization of olefin monomers with MA is described in the examples.

The polymerization reaction of an olefinic monomer with the corresponding substituted maleic anhydrides seems to have been successful when the monomer was the solvent, but was a non-solvent for the copolymer. Usually equimolar quantities of monomers were used with such radical initiators as peroxy or azo compounds. One paper claims the incorporation of dimethyl maleic anhydride and methyl maleic anhydride into copolymers, most prominently styrene copolymers, had been reported (KAZUHIRA, S. and RYUICHI, Y., 1969) but apparently only styrene homopolymer had been obtained (NAKATA, T., 1980).

We are reporting in this paper the successful preparation of alternating copolymers of DMMA/n-butylvinyl ether as well as DMMA/isobutylvinyl ether with AIBN as the initiator (Equation).



EXPERIMENTAL PART

Materials

Dimethylmaleic anhydride (DMMA) (Aldrich Chemical Co.) and maleic anhydride (MA) (Aldrich Chemical Co.) were purified by three sublimations at 0.5 mm and 60°C. The melting point of purified DMMA was 97.5 - 98.0°C. Isobutylvinyl ether (IBVE) and n-butylvinyl ether (BVE) (Aldrich Chemical Co.) were distilled under nitrogen before use. Styrene was washed with 5% aqueous sodium hydroxide solution, dried and distilled under nitrogen at 10 mm immediately before use. Azobisisobutyronitrile (AIBN) was recrystallized three times from dry methanol, m.p. 104.5 - 105.0°C. Toluene was refluxed over sodium overnight and distilled under nitrogen. Methanol was dried over molecular sieves and distilled.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 spectrophotometer, as films cast from chloroform solutions onto sodium chloride plates. ¹³C NMR spectra were measured on a Varian-CFT 20 spectrometer under complete proton decoupling and ¹H NMR spectra were measured on a 60 MHz-24 Hitachi Perkin-Elmer spectrometer. The measurements were carried out at room temperature

as 10% solutions in deuterated chloroform with TMS as the internal standard.

Inherent viscosities were measured in 1,4-dioxane at 25°C. using a Cannon-Fenske viscometer at polymer concentrations of about 0.5 g/dl. The microanalyses were carried out in the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Polymerizations

In a 20 ml Pyrex glass polymerization tube were charged DMMA (1.26 g, 10.0 mmole) and BVE (4.00 g, 40.0 mmole) in 10 ml of toluene. To the clear mixture was added AIBN (40 mg) in 5 ml of toluene. The homogeneous mixture was degassed by three freeze-thaw cycles (nitrogen sweep) and sealed at 0.1 mm. The tube was placed in a constant temperature bath at 50°C. After 5 days, the tube was opened and the viscous contents were dissolved in 20 ml of acetone. The solution was poured into 400 ml of dry methanol, whereby the polymer precipitated. The solid was collected by filtration, washed with methanol and dried at 0.1 mm at 65°C. The yield of polymer was 1.98 g (88% and had an inherent viscosity of 0.25 dL/g (0.5 g/dL solution in 1,4-dioxane at 25°C.). The IR ^{13}C NMR spectra and elemental analysis are shown in Figure 1, Figure 2, and Table 1, respectively.

TABLE 1

Copolymerization of Dimethylmaleic Anhydride (DMMA) with n-Butylvinyl Ether (BVE)^(a)

Amount of Comonomers in Feed				DMMA mole % in feed	Polymer Yield		$\eta_{inh}^{(c)}$ dL/g	Elemental Analysis
DMMA in g	in mmole	BVE in g	in mmole		in g	in wt. % ^(b)		
0.63	5	5.71	57	8	1.10	97	0.32	Calcd.: C, 63.72; H, 7.96 Found
0.63	5	4.57	46	10	1.10	97	0.26	C, 63.55; H, 8.21
1.26	10	4.00	40	20	1.98	88	0.25	C, 64.00; H, 8.09
1.89	15	3.51	35	30	2.03	60	0.24	C, 63.48; H, 8.05
2.52	20	3.01	30	40	1.52	34	0.17	C, 63.55; H, 7.91
1.00	8	0.79	8	50	0.26	15	0.12	C, 63.70; H, 7.96
0.78 ^(d)	8	0.79	8	50 ^(d)	1.49	95	0.63	Calcd.: C, 60.59; H, 7.12 Found: C, 59.58; H, 6.99

(a) Polymerization was carried out in 15 ml of toluene, using 40 mg. of AIBN at 50°C. (5 days).

(b) Calculated on the base of amount of DMMA present in monomer mixture.

(c) 0.5% Solution in dioxane at 25°C.

(d) Comonomer was maleic anhydride.

The DMMA-IBVE copolymerization was repeated exactly as described above except at different comonomer compositions. These results are shown in Table 2.

TABLE 2
Copolymerization of Dimethylmaleic Anhydride (DMMA) with Isobutylvinyl Ether (IBVE)^(a)

Amount of Comonomers in Feed				DMMA mole % in feed	Polymer Yield		η_{inh} ^(c) dL/g	Elemental Analysis for (C ₁₂ H ₁₈ O ₄) _n Calcd.: C, 63.72; H, 7.96 Found
DMMA in g	DMMA in mmole	IBVE in g	IBVE in mmole		in g	in wt. % ^(b)		
0.32	2.5	4.11	41	6	0.42	73	0.12	C, 63.86; H, 8.28
0.63	5	3.90	39	13	0.85	75	0.13	C, 63.77; H, 8.21
1.81	15	7.39	74	16	2.73	84	0.22	C, 63.33; H, 8.15
1.26	10	3.44	34	23	1.34	60	0.12	C, 63.44; H, 7.96
1.89	15	3.04	30	33	1.32	39	0.15	C, 63.50; H, 8.15
2.51	20	2.59	26	43	0.92	20	0.12	C, 63.51; H, 8.20
1.47	15	0.76	8	66 ^(d)	1.36	78	0.62	Calcd.: C, 60.59; H, 7.12 Found: C, 57.35; H, 7.00

(a) Polymerization was carried out in 15 ml of toluene, using 40 mg of AIBN at 50°C. (5 days).

(b) Calculated on the base of the amount of DMMA present in the comonomer mixture.

(c) 0.5% Solution in dioxane at 25°C.

(d) Comonomer was maleic anhydride.

RESULTS AND DISCUSSION

Alternating copolymers of DMMA with BVE or IBVE were prepared in toluene solution with AIBN as the initiator. IR, ¹H NMR and ¹³C NMR spectroscopy confirmed that these copolymers prepared under a variety of conditions are indeed alternating copolymers. A summary of the polymerizations, of the polymerization conditions and the characterization of the polymer is presented in Table 1 for DMMA-BVE copolymers and in Table 2 for DMMA-IBVE copolymers.

The polymer composition calculated from the elemental analysis in both copolymer systems shows that the polymers have exactly alternating structures regardless of the feed ratio of the monomers. The yield of the copolymers of DMMA-BVE are given with respect to DMMA (the comonomer of lower concentration in the feed composition) and the inherent viscosity values of the alternating copolymers are about 0.32 dL/g as compared to the 0.6 dL/g for the MA-BVE copolymer prepared under comparable conditions. Exactly alternating copolymers were obtained also for the DMMA-IBVE system with an inherent viscosity as high as 0.22 dL/g. (MA-IBVE alternating copolymer obtained under similar conditions had a η of about 0.6 dL/g.)

The structure of the copolymers of DMMA-BVE (and DMMA-IBVE) were confirmed by their IR (Figure 1), ¹H NMR and ¹³C NMR spectra (Figure 2). The IR spectra exhibited characteristic IR absorption peaks at 1865 cm⁻¹ and 1785 cm⁻¹ which represents the anhydride carbonyl bands and absorptions at 1240 cm⁻¹ and 960 cm⁻¹ showing the cyclic anhydride and 1100 cm⁻¹ the alkyl ether function. The ¹H NMR spectrum shows the characteristic chemical shift values of the methine and methylene protons calculated to the ether oxygen ($\delta = 3.5$ ppm), the methylene regions and the methyl region of the dimethylsuccinic anhydride portion

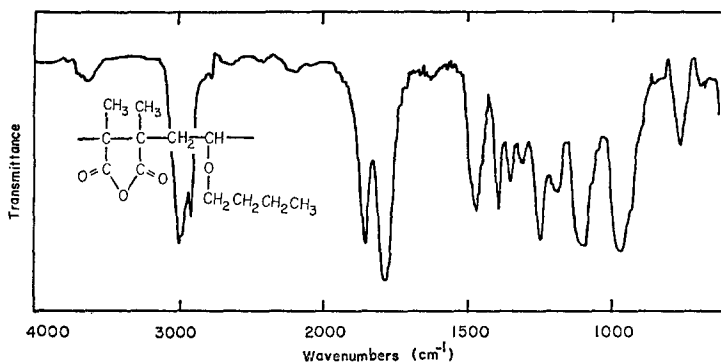


Figure 1: IR Spectrum of DMMA-BVE Copolymer

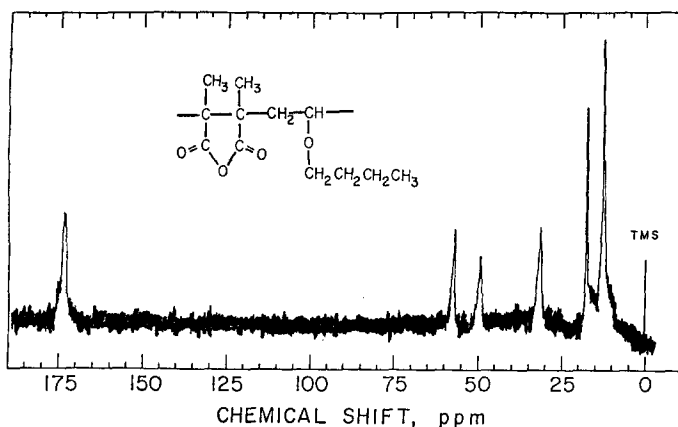


Figure 2: ¹³C NMR Spectrum of DMMA-BVE Copolymer

($\delta = 1.4$ ppm), the chain methylene ($\delta = 1.6$ ppm) and the terminal methyl group ($\delta = 0.9$ ppm). Figure 2 shows the ¹³C NMR spectra of the DMMA-BVE copolymer with the chemical shifts being typical of the carbonyls ($\delta = 173.52$ and 174.25 ppm), methyl ($\delta = 13.81$ and 19.27 ppm), methine ($\delta = 57.70$ and 58.33 ppm), aliphatic methylene ($\delta = 31.51$ to 31.95 ppm), quaternary carbon atoms ($\delta = 49.34$ and 49.42 ppm).

The inherent viscosity, particularly of the DMMA-BVE copolymers, and the film forming capability of the polymers suggests they were of high molecular weight.

The composition of all copolymers calculated from elemental analysis and confirmed by IR and NMR spectroscopy shows an alternating structure irrespective of the feed ratio in the polymerization mixture. It is also remarkable that the rate of copolymerization

increased as the amount of the electron acceptor monomer in the initial monomer mixture was decreased. It was observed that the alternating radical copolymerization is not at optimum conditions as judged by inherent viscosity at the monomer feed ratio of 1:1. This is not a unique observation for it has been reported that the MA-St system, and MA-VA system (SHIROTA, Y. et.al., 1974) are not at optimum copolymerization conditions at a 1:1 feed ratio.

The copolymerization of DMMA was used as the model reaction for the preparation of completely alternating DMMA-ethylene copolymers; the first step in the preparation of pure head-to-head (H-H) PMMA which requires esterification to the methyl ester. Several approaches have been attempted in the past to prepare H-H PMMA, but all attempts up to now have failed to produce pure H-H PMMA. Among the attempts were the cyclopolymerization of methacrylic anhydride and its derivatives and the direct copolymerization of ethylene and DMMA. Under the conditions of the normal ethylene-MA copolymerizations (400 lbs. ethylene pressure), no polymer was obtained even at pressures of 700 - 800 lbs of ethylene; only low molecular weight oils were isolated in low yields which showed some incorporation of DMMA-, but whose composition did not clearly indicate an alternating character in the polymer (YAMADA, A. and VOGL, O., 1978). Furthermore, copolymerization of attempts of styrene and DMMA gave pure polystyrene as observed earlier.

This work was consequently conducted to establish whether the copolymerization involving DMMA was dominated by the steric hindrance of the propagating radical of DMMA which would make it incapable of further polymerization, or whether the failure of propagation in DMMA copolymerization was caused by the poor electron accepting character of DMMA as compared to MA.

The successful alternating copolymerization of DMMA with vinyl ethers has established the fact that steric hindrance does not play a significant part in preventing the copolymerization. We feel that we have further established that for copolymerization purposes the electron density of DMMA is substantially greater than that of MA and that strong electron donating monomers such as vinyl ethers are necessary for the effective copolymerization of DMMA especially when high molecular weight is required. Further work on the copolymerization of DMMA with ethylene is in progress.

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