Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization between Nonconjugated Bicyclic Dienes and Maleic Anhydride

H. Pledger Jr.[a]; B. Butler[a]
[a] Department of Chemistry, University of Florida, Gainesville, Florida

To cite this Article Pledger Jr., H. and Butler, B.(1971) 'Copolymerization between Nonconjugated Bicyclic Dienes and Maleic Anhydride', Journal of Macromolecular Science, Part A, 5: 8, 1339 — 1349
To link to this Article: DOI: 10.1080/00222337108061113
URL: http://dx.doi.org/10.1080/00222337108061113

J. MACROMOL. SCI.–CHEM., A5(8), pp. 1339-1349, December, 1971

Copolymerization between Nonconjugated Bicyclic Dienes and Maleic Anhydride

H. PLEDGER, JR., and GEORGE B. BUTLER

Department of Chemistry
University of Florida
Gainesville, Florida 32601

SUMMARY

Alternating copolymers of maleic anhydride and 5-ethylidene-, 5-methylene-, and 5-vinylbicyclo(2.2.1)-2-heptene were synthesized and found to contain the comonomers in a 1:1 ratio. Evidence is presented which supports a bicyclic structure which incorporates maleic anhydride as part of a six- or seven-membered ring in the repeat unit.

INTRODUCTION

A previous study [1, 2] of the copolymerization between certain nonconjugated bicyclic dienes and maleic anhydride showed that the copolymers contained the diene and maleic anhydride (MA) in a 1:1 molar ratio. The structure which was postulated for the repeating unit contained a nortricyclene unit. This unit was believed to be formed as a result of an intramolecular cyclization step in the propagation mechanism [1]. The evidence for the nortricyclene structure was based on infrared spectra.

This study was undertaken to obtain further evidence for the nortricyclene structure and to extend the copolymerization to other nonconjugated bicyclic dienes. 5-Methylenebicyclo(2.2.1)-2-heptene (MBH)

Table 1. Copolymerizations of

Run No.	Moles MA / Moles diene	Mole initiator / Mole diene	Mole initiator / Mole MA	Mole-% initiator	Mole diene / 1000 ml solvent	Mole MA / 1000 ml solvent	Initiator[a]
1	1:4	0.012	0.050	1.0	0.267	0.067	B
2	1:1	0.020	0.020	1.0	0.167	0.167	B
3	4:1	0.050	0.012	1.0	0.067	0.267	B
4	1:4	0.012	0.050	1.0	0.267	0.067	B
5	1:1	0.020	0.020	1.0	0.167	0.167	B
6	4:1	0.050	0.012	1.0	0.067	0.267	B
7	1:4	0.012	0.050	1.0	0.267	0.067	B
8	1:1	0.020	0.020	1.0	0.167	0.167	B
9	4:1	0.050	0.012	1.0	0.067	0.267	B
10	4:1	0.050	0.012	1.0	0.067	0.267	A
11	4:1	0.050	0.012	1.0	0.067	0.267	A
12	1:1	0.020	0.020	1.0	0.25	0.25	B
13[g]	1:1	0.020	0.020	1.0	2.2	2.2	B
14	2:1	0.010	0.015	1.0	0.25	0.37	B
15	2:1	0.002	0.001	0.064	0.50	1.0	B
16	-	0.010	-	1.0	0.333	-	B

[a] A = azobisisobutyronitrile. B = dibenzoyl peroxide.

[b] MBH = 5-methylenebicyclo(2.2.1)-2-heptene. EBH = 5-ethylidenebicyclo(2.2.1)-2-heptene. VBH = 5-vinylbicyclo(2.2.1)-2-heptene.

[c] B = Benzene. C = Cyclohexanone. THF = Tetrahydrofuran. T = Toluene.

[d] See Experimental section for Method 1. Method 2: diene plus initiator added slowly to solution of MA.

[e] Time in parentheses was time required to add diene-initiator solution.

[f] All copolymers were completely soluble in acetone except as noted.

[g] Gel formation during addition of diene-initiator solution. Copolymer was insoluble in acetone.

copolymerized with MA [1, 2] yielding a 1:1 alternating copolymer. This 1,4 diene contains a terminal carbon-carbon double bond. We wished to determine if 5-ethylidenebicyclo(2.2.1)-2-heptene (EBH), a 1,4 diene which contains two internal double bonds, would undergo the same type of

Bicyclic Dienes with Maleic Anhydride

Diene[b]	Solvent[c]	Method[d]	Time (hr)[e]	Temp. (°C)	% Yield[f]	Mole MA / Mole diene in copolymer	mp (°C)	$\bar{M}_n$
MBH	T	1	4	90.0 ± 0.1	79.8	1.03	200	4200
MBH	T	1	4	"	46.5	1.00	202	3320
MBH	T	1	4	"	100.0	1.00	197	3190
EBH	T	1	4	"	42.0	0.98	213	3420
EBH	T	1	4	"	36.6	1.00	215	3080
EBH	T	1	4	"	78.3	1.00	208	2610
VBH	T	1	4	"	23.3	1.03	197	3130
VBH	T	1	4	"	6.9	1.00	218	3280
VBH	T	1	4	"	17.2	1.03	232	2330
MBH	T	1	9	60.0 ± 0.1	44.9	1.01	203.5	4657
MBH	B	1	9	"	36.3	1.03	202	5016
EBH	C	2	2(0.5)	86-87	28.9	0.98	210	6630
MBH	C	2	0.5(0.25)	80-90	77.4	-	-	-
MBH	C	2	2(0.67)	74-76	56.4	1.00	213.5	1370
MBH	THF	1	3	90.0 ± 0.1	11.8	1.07	104	983
VBH	T	1	24	"	0.0	-	-	-

copolymerization as MBH with MA. Also, we wished to determine if 5-vinylbicyclo(2.2.1)-2-heptene (VBH), a 1,5 diene, would copolymerize with MA by way of an intramolecular cyclization mechanism. If so, the cyclization step would require the formation of a four-membered ring, a more difficult carbocyclic ring to form than a three-membered carbocyclic ring. Consequently, the rate of copolymerization should either be much slower or the reaction route would be different than with MBH.

DISCUSSION AND RESULTS

Table 1 contains data on the copolymerizations between MA and the dienes used in this study and on the resultant copolymers. As expected, the copolymers contained MA and diene in a constant ratio (0.98 to 1.03 moles of MA per mole of diene) regardless of the initial molar ratio of MA to diene. Such a constant composition had previously [1] been found for MBH-MA copolymers.

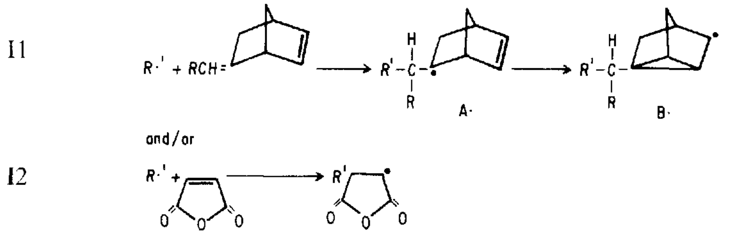
MBH-MA copolymers were made in this study for purposes of structure elucidation and for comparison purposes with EBH-MA and VBH-MA copolymers.

When MBH was copolymerized with MA in tetrahydrofuran (THF), low molecular weight copolymer resulted (Run 15). This copolymer was found to contain 1.07 moles of MA per mole of diene. This higher MA content could have been due to MA end groups affecting the analysis since they would constitute a large percentage of the copolymer.

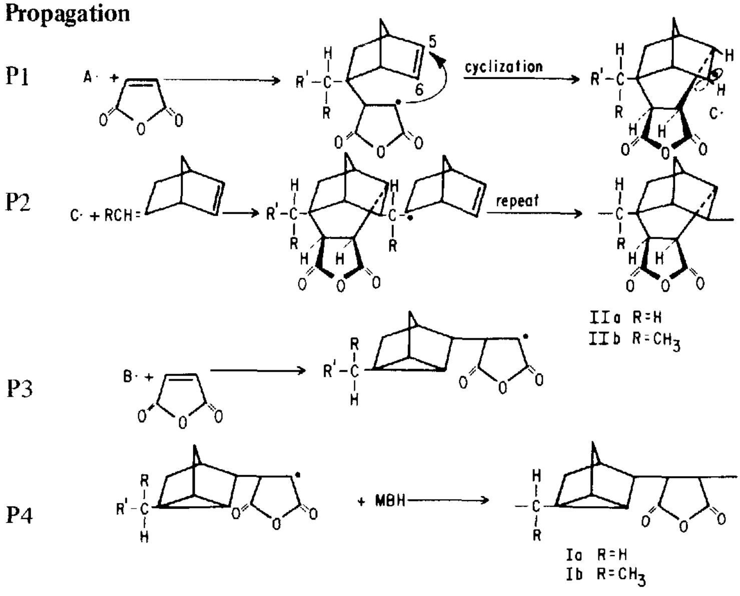
The slowest rate of copolymerization occurred when the initial molar ratio of MBH to MA was 1:1. This is usually not an expected result. In most copolymerizations involving MA where 1:1 copolymers result, the highest rate of copolymerization occurs when the initial molar ratio of MA to diene is 1:1. This result is often explained in terms of an intermediate donor-acceptor (DA) complex [3, 4]. Evidence for a DA complex between MBH and MA was sought by examining the UV and visible spectrum of nine mixtrues of MA and MBH. Mixtures ranging in molar ratios of 1:9 through 9:1 were examined from 240 to 800 mμ. No new absorptions were found. Therefore, either no DA complex was formed between MBH and MA or if one was formed it exhibits an absorption in the same region as MA or MBH and is masked. The latter possibility seems unlikely for two reasons. First, the observed absorbances of the solutions were equivalent to the calculated values for those concentrations. Second, DA complexes are usually found to exhibit absorption maxima at considerably higher wavelength than the acceptor molecule [4, 6]. Therefore, the apparent lack of formation of a DA complex in the MBH-MA system, which would be expected to hold for EBH and VBH as well, allows for an explanation of the observed rates of copolymerization. That is, since growing polymer radicals combine with diene or MA in the propagation step, an excess of one or the other should cause an increase in the rate of copolymerization if the over-all rate is dependent upon the rate of propagation. This is apparently the case since the concentration of initiator was kept constant. These results suggest that Step P1 is faster than P2 and that the over-all propagation rate is controlled by the slow step, P2. It follows that higher concentrations of the diene would increase the over-all propagation rate.

MECHANISM OF COPOLYMERIZATION BETWEEN MA AND MBH OR EBH

Initiation



Propagation

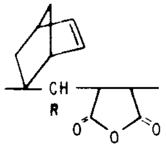


The observed 1:1 copolymer composition is not easily explained if the structures are those proposed later in this paper (IIa and IIb). Formation of these structures would require that cyclized MBH or EBH radical (C) add to MBH rather than MA. Yet, none of these dienes would homopolymerize under the conditions used in this study. If Ia and Ib were the structures of the copolymer repeating unit, then Propagation Step P3 would be involved. However, the evidence is strongly against Ia and Ib and in support of IIa and IIb. Godfrey molecular models of Radical C were constructed. These models show that if a MA molecule approaches the unpaired electron orbital in C from the top, there should be strong electronic repulsion from the MA unit already present. The MA molecule cannot approach from the bottom because the MA unit already present completely blocks its approach. The electronic effect is not experienced by an approaching MBH molecule. The fact that Step P2 proceeds readily in these copolymerizations even though these dienes do not homopolymerize under these conditions may be explained by the overlap of C-Cπ orbitals of MBH with the carbonyl π orbitals of the MA unit, thus stabilizing the transition state. Therefore, the activation energy for attack by MBH is probably much lower than for attack by MA, and also probably much lower than attack by MBH in the analogous homopolymerization, and so a 1:1 copolymer results rather than a 2:1 copolymer.

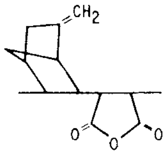
A nortricyclene structure, Ia, had been postulated previously [1] in the repeating unit for MA-MBH copolymer. At that time NMR and completely soluble polymer were not available and the evidence for such a structure was based on a weak absorption in the IR at 3090 cm^{-1}. The present study presents evidence which tends to invalidate such a structure as the predominant one. However, evidence still strongly supports an intramolecular cyclization step, but one involving MA and consequent formation of a six-membered carbocyclic ring for MBH and EBH copolymers and a six- or seven-membered ring for VBH copolymers.

Hart and Martin [7] have found that 1-substituted nortricyclenes absorb at 785-787 cm^{-1} and at 840 cm^{-1}. Roberts and co-workers [8] found that nortricyclene rings absorb at 827 cm^{-1} and cyclopropane at 861 and 1020 cm^{-1}. None of these absorptions appear in the IR spectra of MBH-MA and EBH-MA copolymers.

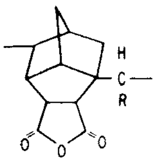
The IR spectra of MBH-MA and EBH-MA copolymers (Runs 1 through 6, 14 and 15) contain very weak absorptions at 3065 and 3060 cm^{-1}, respectively. The absorption at 3065 cm^{-1} probably corresponds to the previously reported absorption at 3090 cm^{-1} for copolymer dispersions. This absorption was previously [1] assigned to the cyclopropyl H on the nortricyclene ring (Structure Ia). However, the absorption at 3060 cm^{-1} in poly-MBH is much stronger, indicating a low concentration of Structure Ia in these copolymers. The 3060 cm^{-1} absorption in EBH-MA copolymer was only about 0.1 as strong as the 3065 cm^{-1} absorption in MBH-MA copolymer, indicating even less of Structure Ib in these copolymers. The



IIIa R = H
IIIb R = CH_3



IVa R = H
IVb R = CH_3



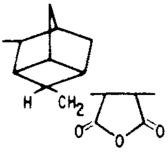
Va R = H
Vb R = CH_3

spectra of the copolymers contained strong, broad absorptions at 1210, 1775, and 1858 cm^{-1} due to cyclic anhydride.

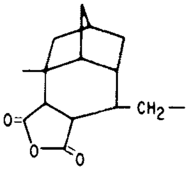
The NMR spectra of the MBH-MA, EBH-MA, and VBH-MA copolymers (Runs 2, 5, 8 and 15, Table 1) were determined in deuterated acetone with TMS as internal standard. The MBH-MA and EBH-MA copolymer spectra contained no resonance signals between 2.0 and 6.0 τ, thus ruling out residual unsaturation and consequently Structures IIIa, IIIb, IVa, and IVb. Monomeric MBH exhibited a singlet (2H) at 3.98 τ (endo double bond protons) and a doublet (2H) at 5.07 and 5.35 τ (J = 12 Hz) (exo double bond protons). Monomeric EBH exhibited a singlet (2H) at 4.10 τ (endo double bond protons) and a multiplet (1H) at 4.32 to 5.05 τ (exo double bond proton). The spectra of the copolymers contained no signals in the 9.2 τ region, thus ruling out Structures Ia and Ib. However, poly-MBH exhibited a sharp singlet (2H) at 9.23 τ, assigned to the two cyclopropyl protons in Structure X. Since the MBH-MA copolymer from Run 15 was of low molecular weight (DP $\simeq$ 4), any signals from nortricyclene protons should have shown up.

These results and arguments favor Structures IIa and IIb with the possibility of a small amount of Structures Ia and Ib in the MBH-MA and EBH-MA copolymers. Alternative Structures Va and Vb do not allow for an explanation for the formation of 1:1 copolymer.

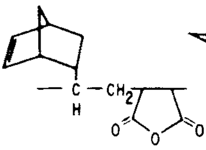
The NMR spectrum of VBH-MA copolymer (Run 8, Table 1) contained a weak signal in the 4.0 to 4.6 τ region which could be due to vinyl protons. However, the protons on double bonds in VBH absorb farther downfield (multiplet 3.70 to 4.15 τ). Therefore, this is weak evidence for VIII and IX. The spectrum contained no features which could be used to distinguish between VI and VII.



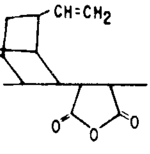
VI



VII



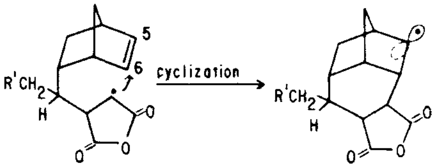
VIII



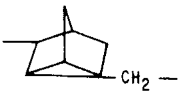
IX

The IR spectrum of VBH-MA copolymer was consistent with Structure VI or VII. It contained strong, broad absorptions at 1210, 1765, and 1850 cm^{-1} due to cyclic anhydride. The spectrum contained no absorptions assignable to carbon-carbon double bonds and no absorption in the 3000 to 3100 cm^{-1} region. These results are in keeping with expectations since results on MBH and EBH copolymers indicated no unsaturation and since VBH could not cyclize to a nortricyclene-type structure. Since four-membered carbocyclic rings are more difficult to form than three-membered carbocyclic rings and since little or no nortricyclene structures are present in MBH and EBH copolymers, Structure VII is favored over VI. Additionally, if Structures VIII and IX are present they constitute a small percentage of the total structure.

Structure VII involves the formation of a six-membered ring but the Radical D undergoing cyclization attacks the bicyclic ring at C6 rather than C5 (as in P1). Radical E, unlike the radical resulting from attack at C6 in P1, is not prone to attack by MA as readily as by VBH because of electronic repulsion and steric bumping as explained above for Radical C. Therefore, 1:1 copolymer results. Attack at C5 during cyclization would produce a seven-membered ring and cannot be ruled out. However, such an attack is probably less favorable and so Structure VII is favored over all other possible structures.



D E



X

The lowered reactivity of VBH over MBH and EBH could be due to differences in rates of initiation. The resultant secondary radical from initiation on VBH should be less stabilized, thus resulting in a lower over-all rate of copolymerization.

The number-average molecular weight of the MBH and EBH copolymers increased as the mole fraction of MA increased. This indicates that MBH (and EBH) is involved in some way in the termination step.

There was little difference between benzene and toluene as solvents for copolymerization. The conversion was lower and the $\bar{M}_n$ higher for benzene, as expected (Run 10 and 11, Table 1). That is, hydrogen transfer to a growing polymer radical causing termination would be more difficult from benzene. Comparison of Runs 3 and 10 shows that azobisisobutyronitrile results in higher molecular weight copolymer than does dibenzoyl peroxide.

Gaylord [9] has used a method of adding a solution of diene and initiator to a solution of MA to obtain high molecular weight copolymers. This method was used in Runs 12, 13, and 14 (Table 1) in an effort to obtain higher $\bar{M}_n$ for MBH and EBH copolymers. Run 13 was made first and resulted in gelation during the addition of the MBH-initiator solution. To avoid the formation of insoluble polymer, the solution concentration of diene and MA was reduced. This resulted in the highest $\bar{M}_n$ obtained in this work for EBH copolymers but a low $\bar{M}_n$ for MBH copolymer.

EXPERIMENTAL

Materials

The dienes were fractionally distilled at atmospheric pressure through a spinning band column, 55 cm band length, which contained an automatic reflux ratio control. The progress of the distillations and purity of the products were followed by vapor phase chromatography using an 8-ft column of diisodecylphthalate on 60/80 Chrom W. The dienes used in the copolymerizations were 99.9+% pure.

Maleic anhydride was purified by sublimation of Fisher Certified maleic anhydride.

Dibenzoyl peroxide was used as obtained (Fisher Certified).

Azobisisobutyronitrile was purified by crystallization from chloroform followed by vacuum drying.

Copolymerization solvents were stored over 3A Linde Molecular Sieves for not less than 24 hr and used without further purification. Benzene and toluene were either Fisher Certified or B and A reagent grade. Cyclohexanone was distilled through a 20-cm Vigreux column before use.

Procedures

Copolymerizations were carried out in a "resin flask" containing a mechanical stirrer, Freidrich condenser with a Drierite guard tube, and a gas inlet tube. The solvent and maleic anhydride were placed in the flask and deoxygenated at the copolymerization temperature (constant temperature bath at 90.0 ± 0.1 or 60.0 ± 0.1°C) by bubbling through purified nitrogen for 15 min while stirring. The diene and initiator were then added and the copolymerization timed from this point with constant stirring. The copolymerizations were terminated by addition of a solution of 1,3-dinitrobenzene or N-phenyl-2-naphthylamine.

When hydrocarbon solvents were used, the copolymer that had precipitated during the reaction was filtered, alternately slurried and filtered several times with dry diethyl ether, and dried at 60°C and less than 0.1 mm pressure for 12 or more hours. When THF and cyclohexanone were used as solvents, the copolymers were precipitated by slowly pouring into vigorously stirred dry diethyl ether. The precipitates were then treated as above.

Homopolymerization of MBH was carried out according to the procedure of Pledger [5]. A 30.0-g (0.283 mole) sample of MBH in 70 g methylene chloride with 0.17 ml boron trifluoride etherate yielded 19.4 g (64.7%) of white powder, mp 187-193°C (capillary tube). The NMR spectrum was determined in CCl_4 solvent with TMS as internal standard.

Melting points of copolymers were determined as the first endotherm using a Perkin Elmer Differential Scanning Calorimeter, Model DSC1A.

Infrared spectra of copolymers were made from KBr discs made with a Wilks Minipress. All spectra were determined on a Beckman IR-8.

Nuclear magnetic resonance spectra were determined with a Varian 60 MHz instrument. Solvents used were either deuterated acetone, carbon tetrachloride, or deuterated dimethyl sulfoxide.

Ultraviolet spectra were determined on a Beckman DK2A spectrophotometer with chloroform solvent.

The mole fraction of maleic anhydride in the copolymers was calculated from titration of excess standard sodium hydroxide with standard hydrochloric acid and sample weight. Titrations were conducted in the cell of a Sargent Model V Oscillometer.

Number-average molecular weights were determined with a Mecrolab Model 302 Vapor Pressure Osmometer.

ACKNOWLEDGMENT

We wish to acknowledge with thanks the support of one of us (H.P., Jr.) by the National Science Foundation in the form of a grant to Emory and Henry College under the College Science Improvement Program and the National Institutes of Health under NIH Grant No. CA06838 for support of this work by providing us with certain of the chemicals and analytical services needed.

REFERENCES

[1] W. D. Beck, H. L. Spell, and H. Pledger, Jr., *J. Macromol. Sci.–Chem.*, **A5**(3), 491 (1971).

[2] H. Pledger, Jr., U.S. Patent 3,143,533 (to Dow Chemical Co.).

[3] S. Iwatsuki, Y. Yamashita, and co-workers, *J. Chem. Soc. Jap., Ind. Chem. Soc. (Kogyo Kagaku Zasshi)*, **67**, 1464, 1467, 1470 (1964); **68**, 1138, 1963, 1967, 2463 (1965); **69**, 145 (1966); *Makromol. Chem.*, **89**, 205 (1965); **102**, 232 (1967); *J. Polym. Sci., Part A-1*, **5**, 1753 (1967).

[4] G. B. Butler, J. T. Badgett, and M. Sharabash, *J. Macromol. Sci.–Chem.*, **A4**(1), 51 (1970).

[5] H. Pledger, Jr., U.S. Patent 3,252,957 (to Dow Chemical Co.).

[6] G. B. Butler and K. C. Joyce, *J. Polym. Sci., Part C*, **22**, 45 (1968).

[7] H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).

[8] J. D. Roberts et al., *J. Amer. Chem. Soc.*, **72**, 3176 (1950).

[9] N. G. Gaylord, U.S. Patent 3,491,068 (1970).

Accepted by editor July 20, 1971
Received for publication July 22, 1971