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The Fundamental Basis for Cyclopolymerization. VII. A Cyclopolymerization Study of Certain Allylcycloalkenes

Jan J. Van Heiningen[a]; George B. Butler[b]
[a] Center for Macromolecular Science, University of Florida, Gainesville, Florida [b] Department of Chemistry, University of Florida, Gainesville, Florida

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The Fundamental Basis for Cyclopolymerization. VII. A Cyclopolymerization Study of Certain Allylcycloalkenes*

JAN J. VAN HEININGEN and GEORGE B. BUTLER

Center for Macromolecular Science and
Department of Chemistry
University of Florida
Gainesville, Florida 32611

ABSTRACT

The cyclopolymerization characteristics of 3-allylcyclopentene, 4 allylcyclopentene, 3-allylcyclohexene, and 4-allylcyclohexene were studied and the extent of their cyclopolymerization by cationic initiation were compared with previously reported solvolysis results involving the same intermediate carbonium ion. The results of this study were also compared with previously reported results on 4-vinylcyclohexene and 1,4-dimethylenecyclohexane. The allylcycloalkenes were also polymerized by metal alkyl coordination catalysts and the extent of cyclization in each case was determined. The polymers derived from these monomers invariably contained polymeric fractions (27 to 99%) which were soluble in nonpolar organic solvents. Calculations based on NMR spectral data indicated the cationic polymers were 68 to 95% cyclized.

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*Taken from the Ph.D. Dissertation of Jan J. Van Heiningen, University of Florida, August 1966.

The extent of cyclization was found to parallel the interolefinic separation in the monomer. Coordination polymerization yielded somewhat lower ratios of cyclizations (54 to 80%) in all cases except for 4-allylcyclohexene. 4-Allylcyclohexene gave only 5 to 54% cyclization. 4-Vinylcyclohexene, 3-allylcyclopentene, and 3-allylcyclohexene produced soluble copolymers with maleic anhydride. Elemental analysis indicated the composition of these copolymers to be 2:1 molar in maleic anhydride and diene units. A cyclic copolymerization mechanism suggested the formation of a multicyclic repeating unit. The other monomers gave crosslinked polymers since maleic anhydride could not be incorporated into a six-membered ring.

INTRODUCTION

In the previous paper of this series [1] the synthesis and spectroscopic (UV, IR, NMR) characterization of 3- and 4-allylcyclopentene and 3- and 4-allylcyclohexene were reported. An extensive UV study was conducted on these and closely related monomers in an effort to determine whether there might be a ground or excited state interaction between the neighboring double bonds in these monomers that could be related to their extent of cyclization. The results of this spectroscopic study failed to support such interactions although many examples of interactions of this type have been reported and studied extensively [2]. It was also a purpose of this investigation to compare the extent of cyclization in cationic-initiated polymerization of these monomers with the extent of cyclization in the solvolytic ring closure experiments referred to earlier [1] in which structurally related carbonium ions were generated by solvolytic techniques.

The monomers were also subjected to metal alkyl coordination initiation and the extent of cyclization determined in each case. In addition, a series of copolymerizations with maleic anhydride were carried out, and evidence obtained to support copolymer compositions of 2:1 molar in maleic anhydride and diene units for those monomers which could yield six-membered rings upon incorporation of maleic anhydride units. Other monomers yielded highly cross-linked copolymers.

Certain monomers somewhat related to those prepared for this study have been studied previously and the extent of cyclization determined in each case. The polymerization of 1,4-dimethylenecyclohexane was reported by Ball and Harwood [3]. Cationic initiation by boron trifluoride produced soluble polymers up to 55% conversion. Analysis of the polymer indicated it was composed of 96% cyclic units.

Butler and Miles [4] have polymerized 4-vinylcyclohexene into soluble, cyclic polymers. Boron trifluoride produced a 28% yield of polymer which was 85% soluble and had $[\eta] = 0.11$ dl/g. Nuclear magnetic resonance data indicated 65% cyclization had occurred. Zeigler polymerization yielded in 20% conversion, a polymer which was 45% soluble, and had $[\eta] = 0.04$ dl/g.

Previous reference [1] was made to the solvolytic ring closure work of Clossen [5], Bartlett [6], and Winstein [7]. The solvolyses of the cyclopentenyl esters have been quite extensively studied. Clossen concludes that solvolysis occurs through anchimeric assistance in the case of the 4-substituted-cyclopentenyl derivative which leads to 97% cyclic product but not in the case of the isomeric 3-substituted compound which leads to 100% noncyclic product [5]. Bartlett has established that there is a symmetric interaction of the double bond, and in addition he has postulated maximum rate enhancements when the double bond is symmetrically oriented with respect to the leaving group [8]. The intermediate may be represented as going through the so-called "π-route" to the nonclassical 2-norbornyl bridged cation. Similar reasoning suggests that greater cyclization should occur in 4-allylcyclopentene than in 3-allylcyclopentene.

Cyclohexenes and cyclopentenes are known to polymerize cationically, but only slowly and in poor yields [9]. Conversely, vinyl compounds can be polymerized much more readily by strong cationic catalysis [10]. It was therefore assumed that initiation took place on the allyl group in the monomers studied. This assumption allows the analogy to be made between the intermediates in cationic polymerization and in the solvolyses.

RESULTS AND DISCUSSION

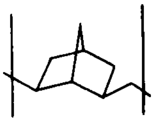
Cationic Initiation

4-Allylcyclopentene was polymerized at -80°C with boron trifluoride as shown in Table 1. An 84% conversion to a polymer which was 96% soluble was obtained. The intrinsic viscosity was 0.05 dl/g and the molecular weight indicated by vapor pressure osmometric determinations was 1786. This molecular weight corresponds on the average to approximately 15 monomer units per polymer chain. Infrared analysis revealed absorptions at 995 and 912 cm^{-1} (vinyl) and a very weak band at 675 cm^{-1} (cis double bond). The NMR spectra confirmed the presence of vinyls, 5.08 and 4.83 δ, and of cis olefinic groupings, 5.66 δ. The respective ratio of the two areas was 0.5 to 0.5 (sp^2 hydrogens) while the sp^3 hydrogen peak had a relative area of 42.6. The polymer structure can be represented by

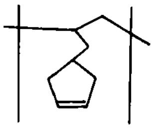
TABLE 1. Polymerization of 4-Allylcyclopentene

Polymer number	Monomer (mmoles)	Solvent (ml)	Initiator			Reaction conditions		Polymer	
			System	[Ti]/[M][a] (mmole)	[Al]/[Ti] (mmoles)	Temp (°C)	Time	Yield (%)	Soluble (%)
IIa	7.5	n-Heptane, 1.5	$TiCl_4$-Al(Et)$_3$	0.01	1	R.T.[b]	30 days	21	N.D.[c]
IIb	7.5	n-Heptane, 1.5	$TiCl_4$-Al(Et)$_2$	0.01	2	R.T.	30 days	28	27
IIc	15.1	n-Heptane, 6	$TiCl_4$-Al(Et)$_3$	0.01	2	50	35 days	32	70
IId	7.5	CH_2Cl_2, 10	BF_3 (gas)			-80	28 hr	84	96
IIf	15.1	n-Heptane, 6	$TiCl_4$-Al(Et)$_3$	0.01	2	R.T.	70 days	17	75

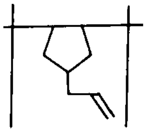
[a] [M] = concentration of monomer in mmoles.
[b] R.T. = room temperature.
[c] N.D. = not determined.



90%

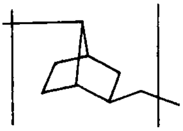


3.3%

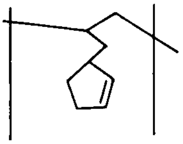


6.6%

The percentage cyclization was calculated from the NMR data by the formula developed by Butler and Miles [4]. The isomeric 3-allylcyclopentene (Table 2) polymerized to a fine white powder in 70% yield. It was found that 73% was soluble and [η] = 0.06 dl/g. If the polymerization was allowed to warm to room temperature before termination with methanol, the yield of polymer increased to 95% but only 29% was then soluble. Infrared analyses revealed that all of the allylic groups had polymerized. This was confirmed by NMR which showed no measurable amount of sp^2 absorption. The experimental sp^3/sp^2 ratio could only be estimated as at least 111/1. Even extremely concentrated polymer solutions revealed no unsaturation. The structures assigned to the polymer on this basis are

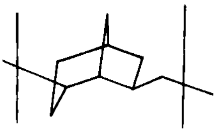


>95%

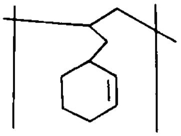


<5%

3-Allylcyclohexene (Table 3) polymerized readily by boron trifluoride in 52% conversion to a 91% soluble polymer. When the polymerization was allowed to warm to room temperature over 18 hr, both the polymer yield (88%) and the solubility (94%) increased. Both polymers proved to be highly cyclized (94 and 91%, respectively) by IR and NMR analysis. The polymers had [η] $\simeq$ 0.05 dl/g and capillary melt temperatures of nearly 160°C. The structures assigned to the polymer on this basis are



91-94%



9-6%

TABLE 2. Polymerization of 3-Allylcyclopentene

				Initiator		Reaction conditions		Polymer	
Polymer number	Monomer (mmoles)	Solvent (ml)	System	[Ti]/[M][a] (mmole)	[Al]/[Ti] (mmoles)	Temp (°C)	Time	Yield (%)	Soluble (%)
IVa	15	n-Heptane, 2.5	$TiCl_4$-$Al(Et)_3$	0.01	1	R.T.[b]	37 days	0.6	N.D.[c]
IVb	15	n-Heptane, 2.6	$TiCl_4$-$Al(Et)_3$	0.01	2	R.T.	37 days	4	N.D.
IVc	15	n-Heptane, 7.8	$TiCl_4$-$Al(Et)_3$	0.03	2	R.T.	40 days	2	N.D.
IVd	7.5	CH_2Cl_2, 5	BF_3 (gas)			-80[d]	24 hr	95	29
IVe	7.5	CH_2Cl_2, 10	BF_3 (gas)			-80	24 hr	70	73
IVf	15	n-Heptane, 6	$TiCl_4$-$Al(i\text{-}Bu)_3$	0.10	2	50	8.5 days	7	75
IVg	10	n-Heptane, 4.5	$TiCl_4$-$Al(Et)_3$	0.14	1	50	16 days	19	81
IVh	15	n-Heptane, 6.0	$TiCl_4$-$Al(i\text{-}Bu)_3$	0.10	2	70	9 hr	9	53
IVi	15	n-Heptane, 6.0	$TiCl_4$-$Al(i\text{-}Bu)_3$	0.10	2	70	21 hr	2.5	N.D.
IVj	15	n-Heptane, 6.0	$TiCl_4$-$Al(i\text{-}Bu)_3$	0.10	2	70	56 hr	5.6[e]	67

IVk	15	n-Heptane, 6.0	$TiCl_4$-$Al(Et)_3$	0.10	2	70	5.3 days	35	7
IVl	15	n-Heptane, 6.0	$TiCl_4$-$Al(i\text{-}Bu)_3$	0.10	2	70	5 days	5	N.D.
IVm	15	n-Heptane, 4.6	$TiCl_4$-$Al(Et)_3$	0.10	1	50	31 days	41	99
IVn	15	n-Heptane, 6.8	$TiCl_4$-$Al(Et)_3$	0.15	1	50	21 days	39	92
IVo	15	n-Heptane, 6	$TiCl_4$-$Al(Et)_3$	0.10	2	50	31 days	31	96
IVp	7.5	CH_2Cl_2, 15	BF_3 (gas)			-80	24 hr	82	76

[a] [M] = monomer concentration, mmoles.

[b] R.T. = room temperature.

[c] N.D. = not determined.

[d] Allowed to warm to R.T. before termination of reaction.

[e] Bath cooled to 40% during polymerization, then reheated to 70°C.

TABLE 3. Polymerization of 3-Allylcyclohexene

				Initiator		Reaction conditions		Polymer	
Polymer number	Monomer (mmoles)	Solvent (ml)	System	[Ti]/[M][a] (mmole)	[Al]/[Ti] (mmoles)	Temp (°C)	Time	Yield (%)	Soluble (%)
IIIa	13.6	n-Heptane, 2.4	$TiCl_4$-Al(Et)$_3$	0.01	1	R.T.[b]	37 days	10	N.D.[c]
IIIb	13.6	n-Heptane, 2.5	$TiCl_4$-Al(Et)$_3$	0.01	2	R.T.	37 days	5	N.D.
IIIc	13.6	n-Heptane, 8.3	$TiCl_4$-Al(Et)$_3$	0.04	2	R.T.	40 days	6	N.D.
IIId	6.8	CH_2Cl_2, 5	BF_3 (gas)			-80[d]	24 hr	88	94
IIIe	6.8	CH_2Cl_2, 10	BF_3 (gas)			-80	24 hr	52	91
IIIf	13.6	n-Heptane 3.1	TiCl-Al(Et)	0.10	1	50	31 days	31	67
IIIg	13.6	n-Heptane 5.4	TiCl-Al(Et)	0.10	2	50	21 days	19	71

[a] [M] = concentration of monomer in mmoles.
[b] R.T. = room temperature.
[c] N.D. = not determined.
[d] After 6 hr allowed to warm to room temperature.

TABLE 4. Polymerization of 4-Allylcyclohexene

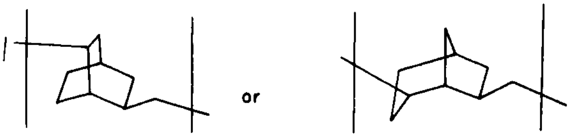
				Initiator		Reaction conditions		Polymer	
Polymer number	Monomer (mmoles)	Solvent (ml)	System	$[Ti]/[M]^a$ (mmole)	$[Al]/[Ti]$ (mmoles)	Temp (°C)	Time	Yield (%)	Soluble (%)
Va	13.6	n-Heptane, 4.1	$TiCl_4$-$Al(Et)_3$	0.01	1	50	7 days	87	68^b
Vb	13.6	n-Heptane, 5.4	$TiCl_4$-$Al(Et)_3$	0.01	2	50	7 days	52	98^b
Vc	13.6	n-Heptane, 5.4	$TiCl_4$-$Al(Et)_3$	0.01	2	R.T.[c]	7 days	51	N.D.
Ve	6.8	CH_2Cl_2, 15	BF_3 (gas)			-80	24 hr	64	51

[a] [M] = monomer concentration in mmoles.

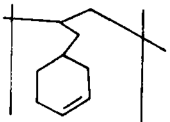
[b] Minimum figure based on isolated soluble polymer after one reprecipitation.

[c] R.T. = room temperature.

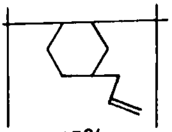
4-Allylcyclohexene (Table 4) was similarly polymerized by boron trifluoride in 64% yield to a polymer which was 51% soluble. Infrared analysis indicated the presence of unreacted vinyl groups (990 and 908 cm^{-1}) and of cis double bonds (650 cm^{-1}). This was confirmed by NMR with absorptions at 5.66, 5.07, and 4.87 δ. Based on the relative areas, the following structures can be assigned:



68%



19%



13%

Analysis of the data for these monomer systems reveals no clear relationship between structure and conversion or ratio of the soluble fraction. There does appear to be a relationship between the monomers and extent of cyclization. Figure 1 reflects this trend. The monomers which were expected to yield exceedingly high amounts of cyclic product, based upon the earlier solvolytic work [5-7], were found to be no better than their 3-allylcycloalkene isomers. Based on the work of Miles and Butler [4], vinylcyclohexene proved to be the poorest monomer for cyclization.

Instead of a symmetrical positioning of the double bond to the reaction site being the most important factor, it appears that the distance between the two double bonds may be significant. Figure 2 records the distances from the =CH— of the vinyl to the nearest carbon of the cis double bond. Calculations were made on Drieding models and in the case of the cyclohexenes the most stable ring conformations were selected. The rough paralleling of the two plots supports the supposition that distance is the major consideration. It must be taken into account that this interpretation is based on a small sample size. More determinations would be necessary to completely verify these results. For example, Polymer IId appears slightly high. Further experiments might show this result to be high so that it might be in better correlation with the other points.

Metal Alkyl Coordination Initiation

Polymerizations initiated by triethyl aluminum-titanium tetrachloride systems have been performed on all of these monomers. The

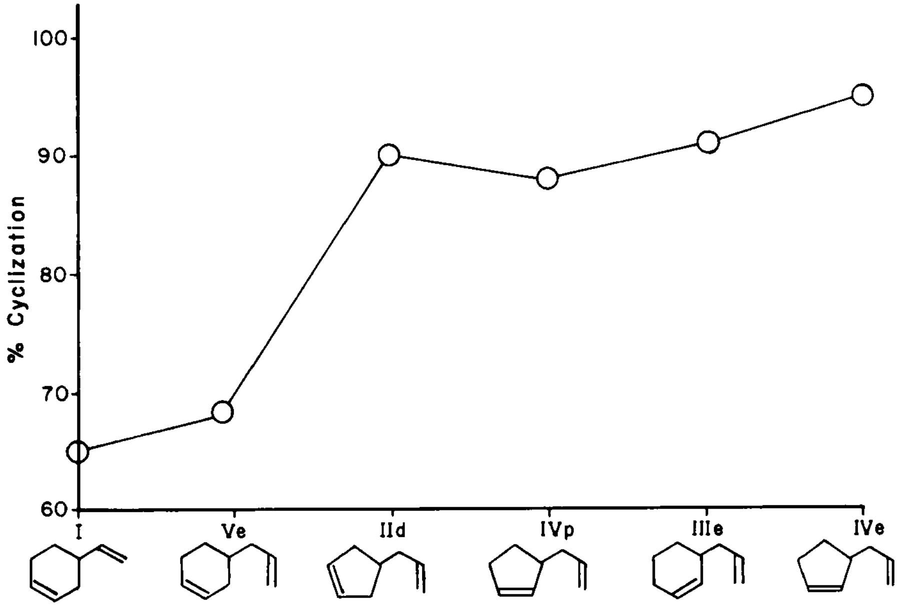


FIG. 1. Relationship of percent cyclization to the monomer polymerized.

polymerization conditions for the respective monomers can be found in the appropriate tables referred to earlier. Since the monomer is believed to be coordinated through its π electron system to a heterogeneous catalyst, it seems likely that other factors besides interolefinic distances must be considered. One factor would be whether the double bonds are dependently or independently coordinated with the catalyst site. These considerations suggest that comparisons with solvolytic data might be extremely risky or even irrelevant. It was for these reasons that the Zeigler polymerizations have been discussed separately and the major comparisons were made with cationic polymerization.

The Zeigler-catalyzed polymerization of all monomers except 4-allylcyclohexene proved to be exceedingly difficult. Since 3-allylcyclopentene was in relative abundance and appeared to be the most difficult to polymerize, a series of definitive experiments were conducted on this monomer.

Based on polymerizations of the 3-allylcycloalkenes, it was evident that at room temperature the conversion was too low and also too slow. To obtain satisfactory amounts of polymer it was necessary

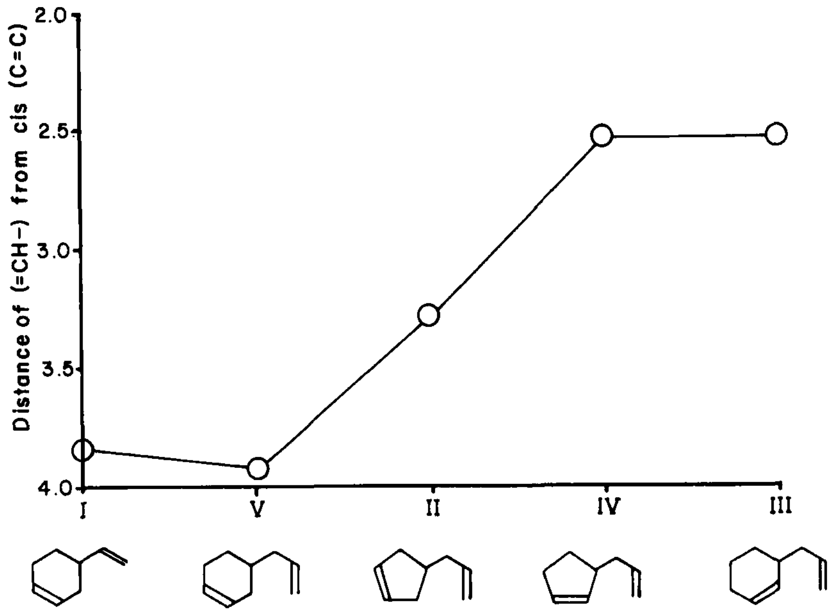


FIG. 2. Separation of olefinic groupings in various monomers.

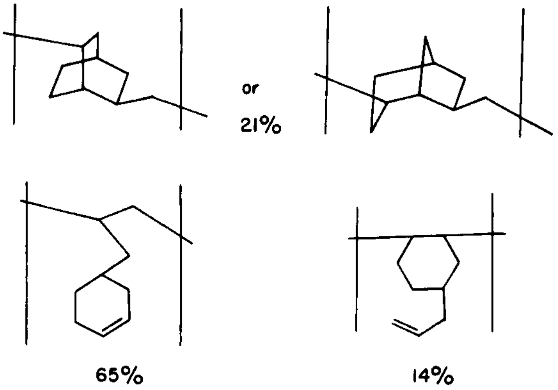
to run the reactions at elevated temperatures and with large amounts of catalyst. The increased conversion was obtained at the expense of the average molecular weight of the polymer. This was expected since it is known that in other Zeigler polymerizations the rate of the terminating steps increases faster than that of the propagating step with elevation of the temperature [11].

3-Allylcyclopentene (Table 2) polymerized optimally at 50°C to 30 to 40% yields of polymer which were greater than 90% soluble. Table 1 summarizes the data for several polymerizations. The preferred catalyst was triethylaluminum:titanium tetrachloride in a 2:1 ratio. The polymers were of very low molecular weight as indicated by intrinsic viscosities of 0.01 to 0.02 dl/g. Vapor pressure osmometric molecular weights were about 1500. Infrared and NMR spectral data disclosed only residual cis unsaturation. The polymers were generally 70 to 80% cyclized.

3-Allylcyclohexene (Table 3) was similarly polymerized at 50°C to give very low molecular weight polymers. The polymers were very soluble in benzene and chloroform (97 and 98%). An intrinsic viscosity of 0.01 and a molecular weight of about 1100 was obtained for one polymer. Infrared and NMR data revealed only cis double bond unsaturation. Calculations indicated the polymers to be about 70% cyclic.

4-Allylcyclopentene (Table 1) polymerized at 50°C to a polymer which was not easily purified since it seemed to cross-link on handling. This monomer gave a better polymer by polymerization at room temperature over a long period of time. A 17% yield of 75% soluble polymer was obtained after 2 months. Infrared and NMR evidence disclosed only 54% cyclization.

4-Allylcyclohexene (Table 4) behaved quite strangely with Zeigler catalysis. Extremely high conversions in short periods of time were obtained either at 50°C or at room temperature. Intrinsic viscosities of 0.1 to 0.45 dl/g indicated the polymers to be of quite high molecular weight. Conversions of 51 to 87% were obtained; conversions would probably have been higher if the polymerization media had not completely solidified. A carefully conducted isolation revealed soluble polymer in excess of 98%. Infrared and NMR spectral data indicated that the extent of cyclization varied from 5 to 54%. Polymerization occurred exclusively through the allyl group except in one case in which analysis indicated the following structure:

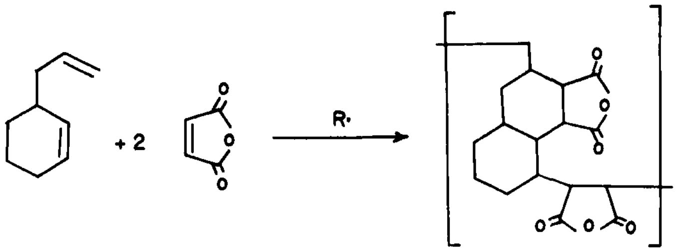


As was mentioned previously, the greater complexity of metal alkyl coordination catalysis makes predictions much less certain. This series of polymerizations revealed no definite trends as the cationic series did. The evidence generally suggested a greater cyclization and solubility with the 3-allylcycloalkenes, however.

Cyclocopolymerization of the Monomers

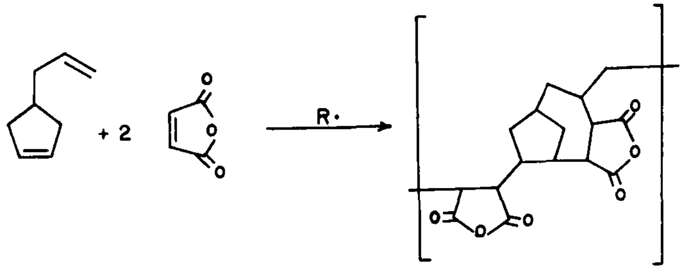
Certain 1,4-dienes such as divinyl ether have been shown to undergo cyclocopolymerization with monomers such as maleic anhydride in a 1:2 molar ratio [12].

The 1,5-diolefins under investigation in this study, for example, 3-allylcyclohexene, were predicted to undergo copolymerization with maleic anhydride to yield the following repeating unit:



In the case of 1,5-diolefins, a six-membered ring could easily be formed by insertion of a maleic anhydride molecule.

The 1,6-diolefins might also be able to cyclocopolymerize, but in this case a seven-membered ring would be required. For example, 4-allylcyclopentene would lead to the following repeating unit:



The results of these copolymerizations are reported in Table 5. All the polymerizations were conducted in sealed vessels with azobisisobutyronitrile as the initiator. Solubility data were determined with dimethylformamide although dimethylsulfoxide was equally as good. The physical properties of the soluble copolymers are reported in Table 6.

The results of this study can be more effectively shown by grouping the monomers by type, either 1,5-dienes or 1,6-dienes, as shown in Table 7.

The polymers appear to arrange themselves cleanly into two separate classes except for the case of 1,4-dimethylenecyclohexane. A closer analysis reveals that although the monomer is a 1,5-diolefin, the preferred site for radical attack would be the less hindered methylene group of the double bond. This means that the intermediate radical would probably react with the diolefin as if it

TABLE 5. Polymers of Some Nonconjugated Diolefins with Maleic Anhydride

Comonomer	Polymer number	Monomer (mmoles)	Maleic anhydride (mmoles)	AIBN[a] (mg)	Benzene (ml)	Time	Temp (°C)	Polymer Yield (%)	Polymer Soluble (%)
4-Vinylcyclohexene	Ig	10	11	20	10	6 hr	70	22	100
4-Vinylcyclohexene	Ih	10	11	20	10	12 hr	70	36	100
4-Vinylcyclohexene	Ii	10	11	20	10	36 hr	70	47	N.D.[b]
4-Vinylcyclohexene	Ij	55	110	200	100	48 hr	70	31	100
4-Vinylcyclohexene	Ik	55	121	200	100	10 days	50	43	100
4-Allylcyclopentene	IIe	3.8	7.8	17.5	11	8 days	50	100	0
3-Allylcyclohexene	IIIh	3.5	7.3	18.6	11	14 days	50	28	94
3-Allylcyclopentene	IVq	3.7	7.9	13.2	11	8 days	50	56	76
4-Allylcyclohexene	Vd	3.4	7.7	17.2	11	7 days	50	83	13
1,4-Dimethylenecyclohexane	VIa	3.8	8.2	15.0	11	7 days	50	99	0

[a] AIBN = α,α'-Azobisisobutyronitrile.
[b] N.D. = not determined.

TABLE 6. Physical Properties of Copolymers of Dienes and Maleic Anhydride

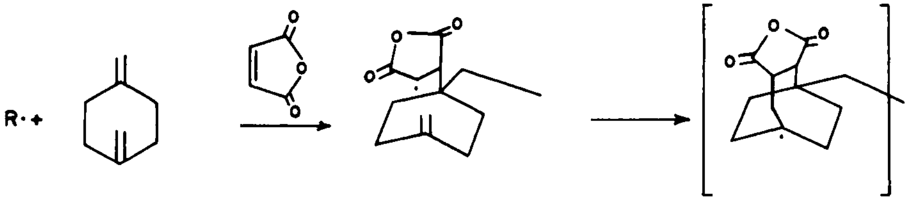
Comonomer	Polymer number	Capillary melt temp (°C)	Intrinsic viscosity	Elemental analysis Calcd (%)[a] C	H	Found (%) C	H
4-Vinylcyclohexene	Ig	235	N.D.[b]	63.15	5.30	62.36	5.70
4-Vinylcyclohexene	Ih	-	N.D.	63.15	5.30	N.D.	N.D.
4-Vinylcyclohexene	Ii	260	N.D.	63.15	5.30	N.D.	N.D.
4-Vinylcyclohexene	Ij	-	N.D.	63.15	5.30	59.14	5.48
Hydrolyzed 4-vinylcyclohexene	Ih	300	0.12	56.46	5.92	56.62	5.82
4-Vinylcyclohexene	Ik	250	0.22	63.15	5.30	60.66	5.48
3-Allylcyclohexene	IIIh	165	N.D.	64.14	5.70	57.93	6.18
3-Allylcyclopentene	IVq	n250	0.17	63.15	5.30	61.58	5.81
4-Allylcyclohexene	Vd	177	N.D.	64.14	5.70	51.73	6.20

[a] Calculated for the 1:2 maleic anhydride, diolefin polymer.
[b] N.D. = not determined.

TABLE 7

Monomer	% Soluble
1,5-Diolefins	
4-Vinylcyclohexene	100
3-Allylcyclopentene	76
3-Allylcyclohexene	94
1,4-Dimethylenecyclohexane	0
1,6-Diolefins	
4-Allylcyclohexene	13
4-Allylcyclopentene	0

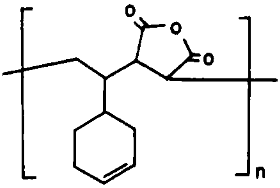
had the following conformation leading to a seven-membered ring rather than to the preferred six-membered ring:



The alternate possibility would place the radical on a primary carbon which is known to be an unfavorable situation [13]. Thus the observed extensive cross-linking can be explained.

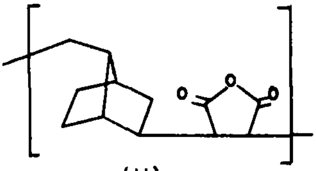
It seems reasonable then that 1,4-dimethylenecyclohexane could be classified under the 1,6-diolefin section since they all had to form seven-membered rings if they were to polymerize by this mechanism. Once this is done, the monomers group themselves nicely into two categories. The 1,5-diolefins each form a high ratio of soluble polymers while the 1,6-diolefins yield largely insoluble polymers.

The ratio of monomers in the repeating unit was deduced from elemental analysis data. There are only three reasonable structures which may be considered as likely repeating units:



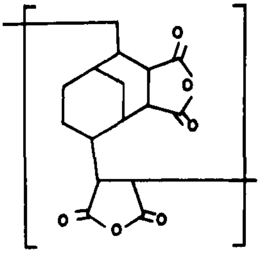
(I)

1:1 unsaturated copolymer



(II)

1:1 saturated copolymer



(III)

2:1 saturated copolymer

Neither 4-vinylcyclohexene [4] nor maleic anhydride [14] is known to homopolymerize readily by free radical initiation. The fact that maleic anhydride prefers to undergo alternating copolymerization and that the diene does not homopolymerize by free radical initiation makes II very unlikely. Structures I and III were considered the most probable units.

Infrared analysis of the copolymer indicated a small amount of unsaturation. Nuclear magnetic resonance indicated the presence of sp^2 hydrogens at 5.6 δ (cis olefin). The ratio of sp^2:sp^3 hydrogens was found to be about 1:23. Calculations for extent of cyclization based on repeating units of either I or III indicated 71% cyclization had occurred.

Elemental analysis clearly indicated that copolymer Structure III had formed. The analytical possibilities for Structures I and III are given in Table 8 along with data for the corresponding acids. The anhydride units are very susceptible to hydrolysis, and consequently it was extremely difficult to prevent anhydride ring opening. The analysis for the completely hydrolyzed copolymer is given to represent the limiting structure if hydrolysis were complete. The expected results should fall between that of the anhydride and that of the acid, if the assignment is correct. A sample of the copolymer was hydrolyzed completely and then analyzed. The data as shown in Table 8 clearly indicate that the majority of the polymer is composed of the 2:1 unit (III). Since some unsaturation did appear in the IR and NMR, it is presumed that there are some 1:1 units (I) in the polymer.

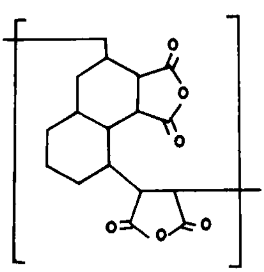
Elemental analyses also indicated 2:1 structures for the copolymers

TABLE 8. Analytical Results on Copolymer of 4-Vinylcyclohexane and Maleic Anhydride

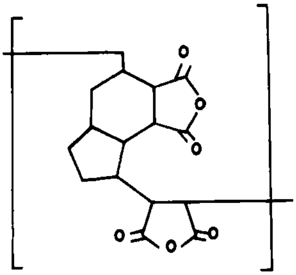
	Calculated		Found	
Polymer type	% C	% H	% C	% H
1:1 Copolymer (anhydride)	69.88	6.84		
2:1 Copolymer (anhydride)	63.15	5.30	62.36	5.70
1:1 Copolymer (acid)	64.27	7.19		
2:1 Copolymer (acid)	56.46	5.92	56.62	5.82

formed by 3-allylcyclohexene and 3-allylcyclopentene. 4-Allylcyclohexene gave a small amount of soluble polymer which analyzed very low in carbon and hence must have included a large amount of maleic anhydride. The polymer was not investigated further.

The soluble copolymers of 3-allylcyclohexene and 3-allylcyclopentene may be represented respectively as IV and V:

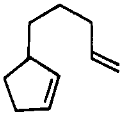


(IV)



(V)

A copolymerization study related to this work has recently appeared in the literature. Imoto [15] found that 4-(cyclohexen-3-yl)-pentene-1 (VI) copolymerized with maleic anhydride to yield a polymer which was insoluble in sodium hydroxide. If this polymer had proceeded by the cyclocopolymerization mechanism, eight- or nine-membered rings would be required. These results are consistent with the conclusions of the present investigation.



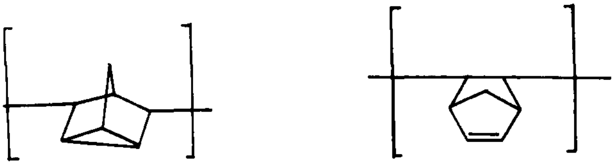
(VI)

Correlation of the Data

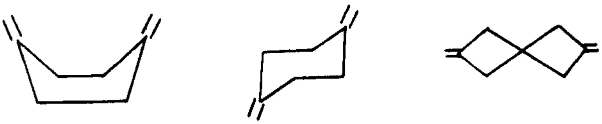
The purpose of this section is to compare the experimental results in the UV study [1] with those obtained in the polymerization study. The objective is to determine if a relationship exists between the UV spectrum of a nonconjugated diolefin and its propensity to cyclopolymerize. Reference will be made to the research of others whenever it will contribute to the contents.

1,4-Dimethylenecyclohexane has been found to exhibit an unusual UV spectrum. This anomaly might be explained by an interaction between the transannularly located double bonds. Ball and Harwood had previously found that this compound could be polymerized into a polymer containing large percentages of cyclic units [3].

Norbornadiene is the only example of a system which definitely shows an interaction in the UV [16] and also cyclopolymerizes [17, 18]. Rabinowitz [17] has shown that free radical polymerization of this monomer yields a polymer containing up to 78% nortricyclane units. The repeating units in the polymer structure are represented by



These two interacting systems have a common feature of limited flexibility. In 1,4-dimethylenecyclohexane the most reasonable conformations are



In a related compound, Orloski found interactions in the system with the ring locked in a boat conformation [19]. The double bonds in norbornadiene are fixed because of the rigid ring structure.

The allylcycloalkenes studied in this investigation were considered likely possibilities to show interactions since the structures were somewhat conformationally restricted due to the alicyclic ring. It was reasoned that the double bonds could never be as far apart as they can in an open chain diene, such as 1,6-heptadiene, which shows no interaction. The high yields of cyclized products in the corresponding unsaturated tosylate solvolyses mentioned previously [5-7] also was a favorable indication.

The UV spectra of the allylcycloalkenes revealed no evidence for stabilization arising from an interaction between the two double bonds. The polymerization of these same monomers generally produced very high amounts of cyclization. On the basis of these experiments, there is definitely no correlation possible since both noninteracting and interacting monomers gave highly cyclized polymers.

Finding cyclic products even though no interaction was detected suggests that the double bonds were not suitably aligned at the moment electronic excitation occurred. A ground state interaction, had it occurred, would have held the double bonds in such a position. There are numerous examples based on UV spectral studies which clearly show that suitably aligned chromophores can interact [2].

With the absence of an interaction, it must be concluded that no ground state interaction is occurring in these flexible systems. Support for this is provided by the absence of any delocalization energy in norbornadiene [20]. There is some doubt expressed by Dewar whether the resonance energy of butadiene is even as large as 2 kcal/mole [21].

Because the noninteracting monomers yielded cyclic polymers, the double bonds (or reactive intermediate) must have resided within the vicinity of one another at some point in time. Why was no evidence found for this?

Apparently, for flexible systems, there is no reason for the double bonds to be close together. When UV light is absorbed, it is so rapid that there is no possibility for the distant olefin to rotate into range through normal molecular rotation. The Franck-Condon principle forbids this [22]. For this reason UV spectroscopy does not seem to be a satisfactory method.

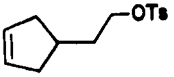
Therefore, unless there is some other compelling factor (rigid ring system, for example) causing olefinic groups to be adjacent to one another, it should not be surprising that no identifiable interaction occurs. It must be concluded that no correlation will be possible in the typical nonconjugated diolefins studied.

The fact that double bonds can interact with vacant p-orbitals in the transition state is well documented by solvolytic rate data where rate enhancements up to 10^{11} times faster than the saturated analog can occur [23].

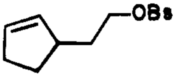
The principle driving force for cyclopolymerization must not reside in a π,π interaction but may result from the energy lowering caused by interaction of the double bond and a developing radical, anion or cation as the case may be. This resonance interaction lowers the energy of the cyclization step relative to that of the linear propagation. Other factors must be taken into account, however. Steric and probability considerations may be more important in some cases.

For polymerizations which yield six-membered ring products, the energetics are apparently closely balanced between cyclic and linear propagation. In the polymerization of diallyl formal, cyclic polymerization is favored by 2.6 kcal/mole [24]. The polymerization of acrylic anhydride [25, 26] and methacrylic anhydride [27] indicates that the cyclic step is about 2.3 kcal/mole higher energy. Predominantly cyclic polymer is obtained since the pre-exponential term favors cyclization by a factor of 200.

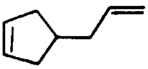
It is interesting to attempt an explanation why allylcycloalkenes were found to polymerize contrary to the expected results. Solvolysis data indicated a high percentage cyclization in VII [6], but not in VIII [5]. Polymerization of the corresponding diolefins, IX and X, revealed that a greater amount of cyclization occurred in X than in IX.



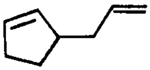
(VII)



(VIII)



(IX)



(X)

An obvious explanation is that the two reactions are not exactly similar. The counterion is known to affect some cationic polymerizations [28]. Possibly this ion $(\mathrm{HO\overset{\ominus}{B}F_3})$ is influencing the reaction.

EXPERIMENTAL

All temperatures are reported uncorrected in degrees centigrade. Molecular weights were obtained on a Mechrolab Model 302 Vapor Pressure Osmometer with a 37°C thermister probe. All determinations were run in benzene solutions. Intrinsic viscosities were run in benzene solutions. Intrinsic viscosities were calculated from efflux times of solutions through a Cannon-Ubbelohde Semimicro Dilution Viscometer set in a 25°C constant temperature bath. Benzene was used as solvent for the homopolymers and dimethylformamide for the copolymers. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

All common solvents and reagents were reagent grade products. The sources were Fisher Scientific Co.; J. T. Baker Chemical Co.; Matheson, Coleman and Bell; and Eastman Organic Chemicals. Boron trifluoride was obtained from The Matheson Co. and used as received. Triisobutylaluminum and triethylaluminum were obtained from the Ethyl Corp. and used as received. Titanium tetrachloride was obtained from the Fisher Chemical Company and distilled before use. Infrared data was obtained on all polymers using potassium bromide pellets. Nuclear magnetic resonance data were obtained on the polymers in chloroform-d_1 and on the copolymers in D_2O or dimethylsulfoxide-d_6. Capillary melt temperatures were recorded on the polymer at the moment visible shrinkage began to occur in the solid powder. This was found to approximate the polymer melt temperature and was much simpler.

Polymerizations

The experimental techniques for the polymerizations conducted in this study may be adequately represented by a single example in each area. The three areas of polymerization were cationic, Zeigler, and free radical copolymerizations.

The physical properties of the polymers and copolymers prepared in this study are given in Tables 6, 9, 10, 11, and 12. By making use of the polymer identification number, polymerization conditions used may be found in earlier tables.

Poly-(4-allylcyclopentene)

A 100-ml., three-necked flask was equipped with a mechanical stirrer, gas inlet, and a reflux condenser-mercury bubbler combination. The apparatus was flamed out once under nitrogen and then cooled in an isopropanol-Dry Ice bath. Ten milliliters of reagent methylene chloride was added to the flask while a slow nitrogen stream was maintained. After 10 min, 1 ml. (0.81 g, 7.5 moles) of 4-allylcyclopentene was added by means of a hypodermic syringe. Following five additional minutes of cooling, the nitrogen flow was replaced by a gentle stream of BF_3 gas. The colorless solution turned orange-brown almost immediately. The BF_3 gas flow was terminated after 9 min and the equipment was sealed with glass stoppers. The flask was stirred for 4 hr, sealed, and stored in a large Dewar flask containing isopropanol-Dry Ice for 24 hr. At this

TABLE 9. Physical Properties of Soluble Polymers of 4-Allylcyclopentene

Polymer number	Capillary melt temp (°C)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental analysis			
				Calcd (%)		Found %	
				C	H	C	H
IIc	67	N.D.[a]	N.D.	88.82	11.18	80.86	10.57
IId	157	0.050	1786	88.82	11.18	88.92	11.10
IIf	55	0.175	N.D.	88.82	11.18	88.80	11.14

[a] N.D. = not determined.

TABLE 10. Physical Properties of Soluble Polymers of 3-Allylcyclopentene

Polymer number	Capillary melt temp (°C)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental analysis				
				Calcd (%)		Found (%)		
				C	H	C	H	O
IVd	180	0.08	3073	88.82	11.18	83.39	10.91	5.57
IVe	174	0.06	7464	88.82	11.18	83.65	10.42	5.62
IVf	120	N.D.[a]	N.D.	88.82	11.18	83.65	10.42	5.62
IVg	102	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVh	112	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVi	129	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVj	19	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVk	59	N.D.	N.D.	88.82	11.18	N.D.	N.D.	N.D.
IVm	63.5	0.02	1471	88.82	11.18	88.73	11.20	N.D.
IVn	58	0.01	1629	88.82	11.18	87.32	11.18	4.38
IVo	64	0.02	1567	88.82	11.18	88.76	11.23	N.D.
IVp	153	0.06	2040	88.82	11.18	86.59	11.12	2.49

[a] N.D. = not determined.

TABLE 11. Physical Properties of Soluble Polymers of 3-Allylcyclohexene

Polymer number	Capillary melt temp (°C)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental analysis			
				Calcd (%)		Found (%)	
				C	H	C	H
IIId	167	0.050	2376	88.45	11.55	88.36	11.58
IIIe	155	0.056	3946	88.45	11.55	88.29	11.48
IIIf	75	0.014	1148	88.45	11.55	88.49	11.59
IIIg	80	0.012	1924	88.45	11.55	88.29	11.60

TABLE 12. Physical Properties of Soluble Polymers of 4-Allylcyclohexene

Polymer number	Capillary melt temp (°C)	Intrinsic viscosity	Vapor pressure molecular weight	Elemental analysis			
				Calcd (%)		Found (%)	
				C	H	C	H
Va	67	0.11	N.D.[a]	88.45	11.55	88.56	11.46
Vb	76	0.18	5,209	88.45	11.55	88.50	11.47
Vc	115	0.45	>10,000	88.45	11.55	88.25	11.60
Ve	110	0.02	2,663	88.45	11.55	88.45	11.52

[a] N.D. = not determined.

time the flask contained orange-brown liquid (viscous) and traces of solid. The polymer was isolated by introduction into the flask of 50 ml of reagent methanol already cooled to -70°C. The polymer immediately precipitated as a fine white polymer. The polymer slurry was transferred into a beaker with methanol until the total volume reached 350 ml. Then the slurry was stirred magnetically for 1 hr, allowed to stand overnight, filtered, and dried 24 hr under vacuum at 50°C to yield 0.68 g (84%) of white polymer. The polymer was treated with 20 ml of cold chloroform, filtered free of insoluble material (0.03 g, 4%), and reprecipitated by dropwise addition to 350 ml of stirred methanol. Filtration, washing, and drying yielded 0.61 g of white solid. Following a second reprecipitation, the following data were obtained: capillary melt temperature 157°C, intrinsic viscosity of 0.05 in benzene, molecular weight 1786. The IR data revealed the following absorption bands: 2940 and 2870 cm^{-1} (C–H), 1650 cm^{-1} (C=C), 1460 cm^{-1} (CH_2), and 990 and 905 cm^{-1} ($CH{=}CH_2$). The NMR determined ratio of sp^3 to sp^2 hydrogens was 42.6:1.

Analysis: Calculated for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.92; H, 11.10.

Poly-(3-allylcyclohexene)

All of the following equipment was flushed overnight in a dry box by a rapid nitrogen flow. All loading operations were conducted in the same inert atmosphere. A specially constructed polymerization bottle consisting of a 24/40 Ŧ top and a 50 ml 24/40 Ŧ bottom was charged with 2.7 ml (1.35 mmoles) of a 0.5 M $TiCl_4$ solution in n-heptane and 2.7 ml (2.70 mmoles) of a 1.0 M triethylaluminum solution in n-heptane. The dark brown precipitate was aged only a few minutes and then 2.0 ml (1.65 g, 13.6 mmoles) of 3-allylcyclohexene (freshly distilled from CaH_2) was added to the slurry. The bottle was then wired shut and placed in a constant temperature bath at 50°C. The bottle was regularly shaken a few minutes each day until isolation, 21 days later. Isolation of the polymer was achieved by pouring the contents of the bottle slowly into 300 ml of magnetically stirred methanol. The bottle was washed out with an additional 50 ml of nonsolvent. After stirring for 1 hr, the dark brown, cloudy solution was allowed to stand overnight. The resulting clear, light brown solution was heated on a steam bath briefly, cooled to room temperature, and filtered to yield 0.32 g (19.4%) of white polymer. The polymer was taken up in 20 ml of chloroform, filtered free of insoluble material (0.01 g, 3%), and twice reprecipitated by dropwise addition to stirred methanol. Yield: 0.25 g of white polymer with the following properties—capillary melt temperature of 80°C, intrinsic viscosity of 0.01 in benzene, molecular weight 1924. The IR data revealed the following absorption bands: 3030 cm^{-1} (CH=), 2930 and 2860 cm^{-1} (C–H), 1445 cm^{-1}(CH_2), and 670 cm^{-1} (CH=CH out-of-plane). The NMR determined ratio of sp^3 to sp^2 hydrogens was 22.7:1.

Analysis: Calculated for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.60.

Copolymer of 4-Vinylcyclohexene and Maleic Anhydride

A polymerization bottle was charged with 5.9 g (55 mmoles) of freshly distilled 4-vinylcyclohexene (bp 55°C/63 Torrs), 11.9 g (121 mmoles) of recrystallized maleic anhydride, 0.2 g of recrystallized azobisisobutyronitrile, and 100 ml of reagent grade benzene. Nitrogen was slowly bubbled through the solution for 5 min, then the bottle was sealed and placed in a 50°C constant temperature bath for 10 days. The polymerization vessel contained white polymer and a light yellow solution. The mixture was poured into 1 liter of a 50:50 mixture of ethyl ether:petroleum ether. The resulting polymer was filtered and dried in vacuum to yield 7.13 g (42.7% conversion, based on a 2:1 maleic anhydride:diene copolymer). The copolymer was dissolved in dimethylformamide (100% soluble) and reprecipitated by addition to a stirred 50:50 ether:petroleum ether solution. The polymer had the following properties: capillary melt temperature greater than 250°C, intrinsic viscosity of 0.22 in dimethylformamide. The IR spectrum of the polymer revealed absorption bands as follows: 2930 and 2870 cm^{-1} (C—H); 1865 and 1780 cm^{-1} (five-membered ring anhydride); and 1215, 1060, and 910 cm^{-1}. The NMR-determined ratio of sp^3 to sp^2 hydrogen was 23:1.

Partial hydrolysis had occurred during purification. The limiting analysis for completely hydrolyzed 2:1 copolymer would be: Calculated for $C_{16}H_{20}O_8$: C, 56.46; H, 5.92.

Analysis: Calculated for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 60.66; H, 5.48.

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