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Copolymerization of Dienophiles and Bicyclic Dienes

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SUMMARY

Copolymers of 5-methylenebicyclo(2.2.1)-2-heptene and maleic anhydride were prepared by free radical copolymerization. Copolymers of constant composition with an alternating arrangement of comonomers but of varying solubilities, degrees of cross-linking, and molecular weights were obtained. The effects of comonomer feed ratios, comonomer concentration, initiator concentration, and temperature were studied. Copolymers of 5-methylenebicyclo(2.2.1)-2-heptene and maleimide, bicyclo(2.2.1)-2,5-heptadiene and maleic anhydride, and 1,2,3,4,4a,5,8,8a-octahydro-2-methylene-1,4,5,8-dimethanonaphthalene and maleic anhydride were also investigated.

INTRODUCTION

Many studies have been reported on the copolymerization of maleic anhydride with olefins. However, few examples are known wherein the olefin will copolymerize with maleic anhydride but will not homopolymerize.

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We have made a study of the dibenzoylperoxide initiated copolymerization of several dienophiles with bicyclic dienes, none of which will homopolymerize under the influence of dibenzoyl peroxide. This report is concerned with results on the copolymerization between maleic anhydride (I) and 5-methylenebicyclo(2.2.1)-2-heptene (II), I and bicyclo(2.2.1)-2,5-heptadiene (VII), maleimide and II, and 1,2,3,4,4a,5,8,8a-octahydro-2-methylene-1,4,5,8-dimethanonaphthalene and I.

DISCUSSION AND RESULTS

Copolymerization of Maleic Anhydride (I) and 5-Methylenebicyclo (2.2.1)-2-heptene (II)

Studies in this laboratory have shown that II will not homopolymerize under the influence of dibenzoylperoxide, ultraviolet (UV) light, or anionic initiators such as sodium naphthalene. However, this diene will homopolymerize under cationic initiation, and this study will be the subject of a future report.

The ratio of comonomers in the copolymer should be 1:1 since neither I nor II will homopolymerize under radical initiating conditions. The monomer reactivity ratios due to Alfrey and Goldfinger [1] should be zero. These ratios have not been experimentally determined in this work. Evidence is presented which indicates that the copolymers do indeed contain the comonomers in a 1:1 ratio. Furthermore, these are necessarily arranged in an alternating manner. Table 1 contains data which show that the comonomer ratios in the copolymers are 1:1 regardless of the comonomer ratios initially (compare runs made for 4 hr). These same data also show that the copolymer composition is constant and independent of the rate of copolymerization. This independence also holds true with a constant comonomer feed ratio.

Table 2 contains data which confirms that dilution affects the rate of copolymerization but has no effect upon the copolymer composition. This dilution effect upon reaction rate is not due to a reduction in initiator concentration, at least with respect to I. The mole % initiator was kept constant with respect to I within a given comonomer feed ratio.

Initiator concentration apparently had no influence upon the comonomer

Table 1. Copolymerization of Maleic Anhydride (I) and 5-Methylenebicyclo(2.2.1)-2-Heptene (II) in Xylene at 90°[c,d]

		Reaction		Copolymer	
$\frac{\text{Moles I}}{\text{Moles II}}$	$\frac{\text{Moles } Bz_2O_2}{\text{Moles I}} 100$	Time (hr)	%[b]	$\frac{\text{Moles I}}{\text{Moles II}}$	Solubility[c] (g)
1/5	1.0	4	88.0	0.98/1.00	19.3
1/5	1.0	3	89.8	0.97/1.00	–
1/5	1.0	2	81.5	0.97/1.00	–
1/5	1.0	1	58.0	1.00/1.00	–
1/5	1.0	0.5	42.8	0.99/1.00	50.0
1/2	0.4	4	81.6	0.98/1.00	–
1/2	0.4	3	84.2	0.99/1.00	–
1/2	0.4	2	68.2	1.02/1.00	–
1/2	0.4	1	45.0	0.97/1.00	–
1/1	0.2	4	38.8	0.98/1.00	–
1/1	0.2	3	38.3	1.04/1.00	18.9
1/1	0.2	2	23.1	0.98/1.00	–
1/1	0.2	1	18.5	1.01/1.00	52.8
2/1	0.1	4	35.9	1.00/1.00	26.9
2/1	0.1	3	39.1	0.99/1.00	25.8
2/1	0.1	2	37.9	1.00/1.00	–
2/1	0.1	1	20.8	1.01/1.00	–
2/1	0.1	0.5	16.3	1.02/1.00	70.8

[a] The solution concentration was 1.0 mole II/1000 ml xylene.

[b] These values were determined by potentiometric titration of unreacted maleic anhydride.

[c] This is the grams of copolymer extractable by tetrahydrofuran from 100 g copolymer.

[d] For all tables the "runs" referred to in the text are numbered from the top line of data downward.

ratio in the copolymer. In addition to the data in Table 1 which supports this supposition, whenever the initiator concentration was doubled with respect to I but the comonomer ratio, temperature, reaction time, and solution concentration were kept constant, the composition remained constant. The reaction rate increased from 38.2 to 54.2% reaction.

Table 2. Effect of Dilution Upon Reaction Rate and Copolymer Composition[a]

Feed, Moles I / Moles II	Xylene (ml) / 1.0 Mole II	Reaction (%)	Copolymer Moles I / Moles II	Copolymer Solubility[b]
1/5	1000	89.8	0.97/1.00	19.3[c]
1/5	3000	70.3	1.02/1.00	100.0
1/1	1000	38.3	1.04/1.00	18.9
1/1	2000	31.8	0.99/1.00	32.6
2/1	1000	39.1	0.99/1.00	25.8
2/1	2000	29.2	1.00/1.00	100.0
2/1	3000	28.4	1.01/1.00	100.0

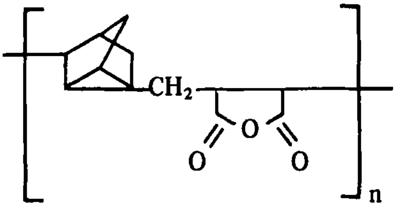
[a] All runs were made for 3 hr except the one indicated.

[b] This is the grams of copolymer extractable by tetrahydrofuran from 100 g copolymer.

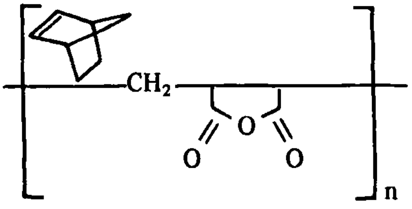
[c] Run 4 hr.

Additional evidence for the 1:1 comonomer ratio in the copolymers resulted from the synthesis of derivatives. Reaction of the copolymer with ammonia and aniline would be expected to leave the backbone of the copolymer intact; only the pendant anhydride linkage should be affected. Nitrogen analysis on the ammonated copolymer supported the proposed 1:1 composition and IR analysis confirmed that the backbone was unaffected. IR showed that the repeating unit contained pendant carboxyl and acid amide groups. While the carbon analysis and nitrogen analysis of the copolymer resulting from amminolysis with aniline are 0.9 and 0.6% lower, respectively, than the theoretical values for a 1:1 copolymer, they do support such a composition. The theoretical values do not take into account the end groups.

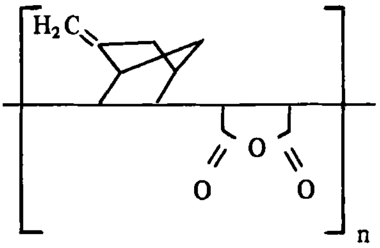
The arrangement of the comonomers in the repeating unit could theoretically be any or all of those represented by III, IV, and V. IR analyses tend to exclude V since no absorption occurred in the 800 to 900 cm^{-1} region (hydrogen out-of-plane deformation for $>C=CH_2$ groups). The copolymers had a weak, sharp absorption at 3090 cm^{-1} which could be due to C–H stretch on a carbon carbon double bond or on a cyclopropane ring. The absorption was decreased (>95%) by brominating the suspended copolymer in CCl_4 at room temperature. Unfortunately, this result is of little value because the cyclopropane ring could open under these conditions. Normally, the difficulty of distinguishing between III and IV could be resolved on the basis of other absorptions. However, the broad bands of the anhydride portion of the copolymer mask the region (1665 cm^{-1}) where these occur. Structure III is indicated by the fact that C–H stretch on a cyclopropane ring with the type of substitution the ring has in III is assigned in the 3050-3090 cm^{-1} range of Liebman [2], whereas C–H stretch on –CH=CH– occurs at lower frequencies (3010-3040 cm^{-1}) as reported by Bellamy [3]. The absorption at 3090 cm^{-1} coincides exactly with that in the copolymer of I and bicyclo(2.2.1)-2,5-heptadiene and that in poly[5-methylene-bicyclo(2.2.1)-2-heptene], which is almost certainly a poly(nortricyclene). IR examination of thick films of the latter polymer in the 1660 cm^{-1}



III



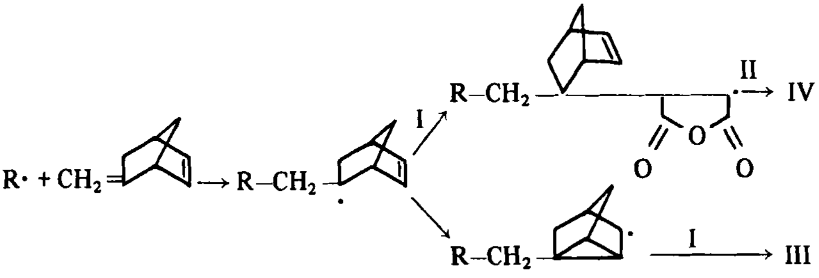
IV



V

region indicated the complete absence of C=C groups. This will be covered in a future report. Catalytic hydrogenation of the copolymer was of no help in distinguishing between III and IV, even though the absorption at 3090 cm^{-1} was reduced, since the cyclopropane ring could conceivably open. Addition of maleic anhydride and dibenzoylperoxide to noncross-linked copolymer in xylene failed to give any cross-linking after 4 hr at 90°. This was evidenced by the lack of any change in the melting point or solubility of the copolymer. Since, as solubilities indicate (Table 1), the cross-linking increases with time of reaction, these results tend to exclude IV and further indicate that cross-linking during copolymerization must not involve Structure IV.

The following mechanism of copolymerization is proposed and is consistent with our data:



We prefer the route that involves an addition-cyclization process [4]. We include the alternate route because our data does not exclude it. The bridging process should be aided by the less steric inhibition involved when the newly generated radical (resulting from bridging) attacks Monomer I than when the primarily formed radical attacks Monomer I.

The effect of dilution upon the copolymerization should be to cause a change in the degree of cross-linking, the degree of copolymerization, and the rate of copolymerization. The latter effect has already been discussed. It has previously been shown that dilution had no effect upon comonomer ratios in the copolymer.

The change in the degree of cross-linking is reflected in the change in solubility of the copolymer in tetrahydrofuran. The data in Table 2 clearly show that less cross-linking occurs at lower monomer concentrations when the comonomer ratios in the feed are kept constant. That is, solubility of the copolymer increases with increasing dilution.

The change in the degree of copolymerization would be evidenced by a change in viscosity molecular weight. Such a change in molecular weight would, of course, be reflected in changes in the limiting viscosity number (intrinsic viscosity). A few limiting viscosity numbers have been tabulated in Table 3. A twofold dilution did cause a decrease in molecular weight. This decrease could have been due to a reduction in the number of copolymer molecule chains joined by a cross-link.

Table 3. Effect of Dilution upon Limiting Viscosity Number of Copolymer I-II in Methyl Ethyl Ketone at 25.00 ± 0.02°

Feed, Moles I / Moles II	Xylene (ml) / 1.0 Mole II	Reaction time (hr)	M.p. (°C)[a]	$[\eta]$	$[\eta]^c$
2/1	2000	3	229	0.258	0.096
2/1	3000	3	211	0.140	0.082
2/1[b]	2000	4	231	0.181	0.112
1/5[d]	3000	3	228	0.099	0.059

[a] These are the temperatures at which copolymer began to melt in a sealed tube.

[b] Reaction conducted at 70° instead of 90°.

[c] This is the limiting viscosity number that would be obtained if viscosities were not determined below 0.1 g/100 ml solution.

[d] This is Copolymer I-VII.

The effect of temperature appears to be one of changing the degree of copolymerization. This is indicated by a decrease in limiting viscosity number when the reaction temperature is raised, Runs 1 and 3, Table 3. A 20° reduction in reaction temperature produced a threefold reduction in reaction rate, but the comonomer ratio in the copolymer was unaffected.

The unusual viscosity effect noted for these copolymers is illustrated by the rather sharp break in the curves in Fig. 1. This break occurs at approximately 0.1 g/100 ml concentration. This is usually the lower limit of concentration at which most investigators determine solution viscosities. Such a break in the plot of viscosity number vs. concentration was first studied and reported by Boyer and Streeter [5] in their work with polystyrene. If polymer molecules were being adsorbed on the walls of the viscometer, such an effect as noted here should be found. However, Cutter and Kimball [6] have shown that when such adsorption occurs, the plot of specific viscosity vs. concentration results in a curve which crosses the concentration axis at a positive value. This test has been applied in Fig. 2.

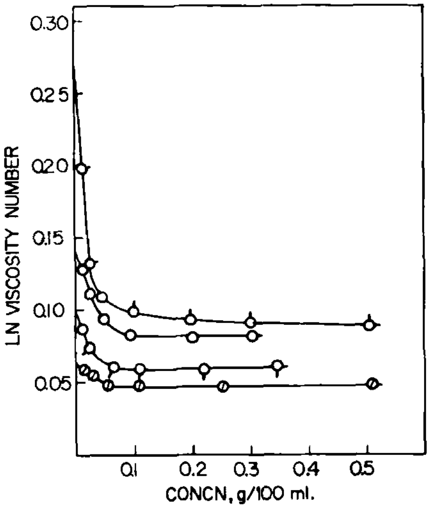


Fig. 1. Viscosity numbers of copolymers in methyl ethyl ketone at 25.00 ± 0.02°. Comonomer ratios I/II in feed (ml xylene solvent used in run): ȯ, 2/1 (2000); o, 2/1 (3000); ♀, 1/5 (3000); ⊖, copolymer I/VII, 1/5 (1000).

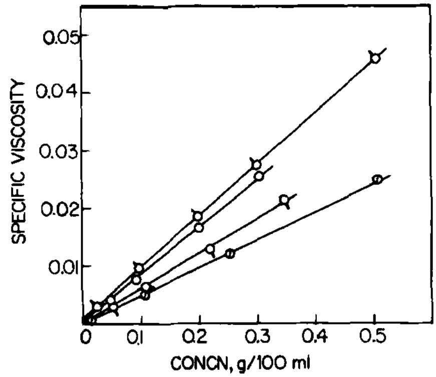


Fig. 2. Specific viscosities of copolymers in methyl ethyl ketone at 25.00 ± 0.02°. Comonomer ratios I/II in feed (ml xylene solvent used in run): ȯ, 2/1 (2000); o, 2/1 (3000); ♀, 1/5 (3000); ⊖, copolymer I/VII, 1/5 (1000).

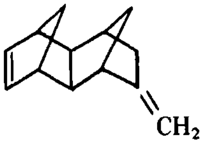
Note that the points lie on a straight line and these lines converge to a point slightly below zero concentration. Therefore, the breaks in the logarithmic viscosity number vs. concentration curves are not apparently due to adsorption effects.

These results, along with those of Boyer and Streeter [5] and Takeda and Tsuruta [7], lead one to question if this is a common phenomenon.

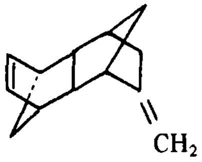
Copolymerization of Maleic Anhydride (I) and 1,2,3,4,4a,5,8,8a-Octahydro-2-methylene-1,4,5,8-dimethanonaphthalene (VI)

This copolymerization proceeded very slowly even though it was conducted at 120-126°. The yield of polymer indicated only 1.9% conversion as opposed to 89.8% for Monomer II under identical conditions except for temperature.

If copolymerization proceeds by bridging as shown above for Monomer II, then VI should give no polymer since no bridging could occur. Therefore, since very little polymerization occurred, this fact lends support to Structure III. If the structure of the monomer is that represented by VIa rather than VIb, then the exo double bond is more hindered to the approach of I than is true in monomer II. However, it does not seem reasonable that this difference in steric inhibition can account for the vast differences in reactivity between VI and II.



VIa



VIb

Copolymerization of Maleimide and 5-Methylenebicyclo(2.2.1)-2-heptene (II)

These two comonomers were copolymerized under conditions comparable to the fifteenth run in Table 1. Elemental analyses indicate the copolymer contains the comonomers maleimide:II in a molar ratio 3:1. The copolymer displayed the same four principal absorptions in the IR as maleimide. These results are in good agreement with those found by Tawney et al., [8] for copolymers of maleimide. They found that maleimide, unlike maleic anhydride, will homopolymerize, thus the higher proportion of maleimide in the copolymer reported here.

Copolymerization of Maleic Anhydride (I) and Bicyclo(2.2.1)-5-heptadiene (VII)

The amount of I in the copolymer varied directly as the amount of I in the feed. This variation is illustrated by the data in Table 4. This is contrary to what was observed for copolymerization of 5-methylene-bicyclo(2.2.1)-2-heptene (II) and I. The molar ratio I:VII in the copolymer appeared also to be dependent upon concentration of comonomers in the solvent, Table 4, Runs 4 and 5.

Table 4. Copolymerization between Bicyclo(2.2.1)-2,5-heptadiene (VII) and Maleic Anhydride (I) at 90° in Xylene

Feed,			Reaction		Copolymer	
$\frac{\text{Moles I}}{\text{Moles II}}$	$\frac{\text{Moles Bz}_2\text{O}_2}{\text{Moles I}}$ 100	Xylene (ml)	Time (hr)	%	$\frac{\text{Moles I}^{a}}{\text{Moles VII}}$	M.p. (°C)[b]
1/5	1.0	1000	3	4.7	0.661/1.00	323
1/5	0.4	1000	3	10.2	0.686/1.00	309
2/1	0.1	1000	3	27.4	0.763/1.00	338
2/1	0.2	1000	3	50.0	0.793/1.00	209
2/1	0.2	6320	3	8.6	1.051/1.00	133

[a] These values are derived by potentiometric titration of hydrolyzed copolymer.

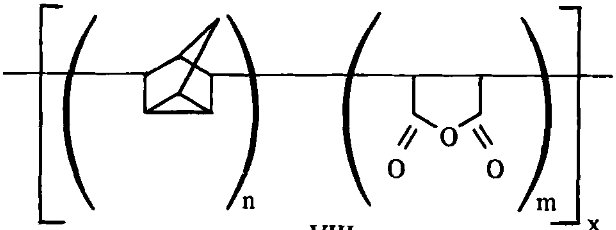
[b] The temperature at which polymer began melting in a sealed tube.

The copolymers were, in every case, very soluble in acetone and tetrahydrofuran, indicating no cross-linking.

The rate of copolymerization was much slower for Comonomer VII than for Comonomer II.

The IR absorption (3090 cm^{-1}) due to C–H stretch on either a double bond or a cyclopropane ring coincided exactly with that of copolymer I-II and homopolymer of II. The remainder of the spectrum was similar to that of Copolymer I-II and in good agreement with the proposed structure (VIII). It is therefore proposed that the repeating unit in this copolymer has Structure VIII.

This copolymer showed the same unusual viscosity behavior as that displayed by Copolymer I-II. The curve of logarithmic viscosity number vs. concentration is included in Fig. 1. This plot gave a limiting viscosity number, $[\eta] = 0.063$ and $[\eta]^* = 0.048$. The curve of specific viscosity



VIII

versus concentration is included in Fig. 2 and indicates no adsorption on the viscometer walls.

EXPERIMENTAL

5-Methylenebicyclo(2.2.1)-2-heptene (II)

The synthesis of this compound has been previously reported [9]. The material used in this study had b.p. 73.0°/172 mm, n_D^{20} 1.4862, d_4^{20} 0.889, and was shown by gas chromatography to contain one component as an impurity in a concentration of 0.5%.

Maleic Anhydride (I)

Maleic anhydride (I) was obtained from Monsanto Chemical Co. and was used without further purification.

Bicyclo(2.2.1)-2,5-heptadiene (VII)

This material was obtained as a 1-gallon sample, stored under nitrogen, from Shell Chemical Co. and contained two impurities as minor constituents, approximately 1.5%.

Maleimide

This compound was synthesized by the procedure of Snyder et al. [10]. Material used in this work had m.p. 92.0-93.5°.

Copolymerization between 5-Methylenebicyclo(2.2.1)-2-heptene (II) and Maleic Anhydride (I)

The apparatus was charged with the correct quantity of I and xylene and heated to 50° while stirring under N_2 until homogeneous. The correct amount of II was added followed by dibenzoylperoxide. The homogeneous solution was immersed in a water bath maintained at 90° and stirred under N_2 throughout. The first evidence of reaction occurred when the solution suddenly became cloudy. The time required to bring the reaction mixture from this cloud temperature to 90° was between 4 and 10 min. The times of reaction reported herein includes this time.

After the elapsed time of heating, the copolymerization was stopped by adding a xylene solution of N-phenyl-2-naphthylamine, which was shown to prevent copolymerization for at least 4 hr. The heterogeneous mixture was cooled to 30°, the copolymer removed by suction filtration, the filter cake beaten 60 sec in a Waring blendor with 250 ml methanol, and filtered. The filter cake was dried to constant weight at 70 to 95° under a pressure of 0.03 to 0.06 mm.

A sample of copolymer prepared by reacting 2 moles I with 1 mole II was analyzed. In no case was the carbon analysis as high as the theoretical value. This was confirmed independently by two analytical laboratories. These low values are believed to be due to incomplete combustion and to the fact that the theoretical values do not take end groups into consideration.

Analysis calculated for $C_{12}H_{12}O_3$: C, 70.5; H, 5.89;), O, 23.5. Found: C, 68.81; H, 5.80; O, 24.77.

Hydrolysis of Copolymers of 5-Methylenebicyclo(2.2.1)-2-heptene (II) and Maleic Anhydride (I)

A weighed sample of I-II copolymer was stirred into a solution of 150 ml pyridine containing 20 ml water. The heterogeneous solution was heated to reflux (100°) whereupon the solution usually become homogeneous. The solution was refluxed 4 hr, cooled to 30°, poured into 150 ml water containing ice, and the solution acidified to pH ~2 with 50% hydrochloric acid. The precipitated polyacid was filtered by suction, washed with 50 ml water, and dried to constant weight at 35° and 0.6 mm. Yields of polyacid ranged between 90 and 100%.

These polyacids did not melt below 360°. Only one was soluble in pyridine, that derived from copolymer from Run 6, Table 2. The others formed fairly stable suspensions in pyridine. They were all insoluble in water.

The polyacid, 0.495 g, which was soluble in pyridine was dissolved in 50% aqueous acetone, about 0.1 g sodium chloride added, and the solution titrated potentiometrically with 0.1 N sodium hydroxide. The first inflection point in the titration curve corresponded to neutralization of the first carboxyl [11] and occurred at pH 6.85, requiring 22.4 ml. A repeating unit,

$C_{12}H_{14}O_4$, containing two carboxyls would require 22.3 ml 0.1 N sodium hydroxide to neutralize the first carboxyl.

Analysis of Copolymer of 5-Methylenebicyclo(2.2.1)-2-heptene (II) and Maleic Anhydride (I)

The copolymers of I-II were hydrolyzed and analyzed as their polyacids by IR techniques. The method involved mixing the powdered sample with pyridine by means of a hypersonic generator to form a uniform, stable suspension and introducing the suspension into a standard IR cell to record the spectrum. All conditions were shown to be reproducible and a standard deviation of ±0.5% was obtained from the results (53.0, 52.7; 53.1, 53.5; 53.2, 52.3; 50.8, 51.0; 54.7, 54.2; 54.2; 51.6, 51.8; 53.0, 51.9 wt % polymaleic acid) of seven duplicate runs.

A sample of copolymer derived from Run 6, Table 2, with an acid content established by titration methods (52.3 wt %) was employed as the standard. About 0.1 g of sample was ground in an agate mortar for 30 min. At this point, a measured portion of the sample was dispersed in water and examined with a 440-power microscope. The grinding operation was continued until practically 100% of the particle diameters measured less than 3 μ. (Experimental results had shown that the true intensity of the 5.9 μ C=O band or the limiting value of the absorptivity was practically attained when the particle diameters measured 3 μ or less.)

A stable suspension of the sample was obtained by mixing 0.075 g in 5 ml pyridine with a hypersonic generator. The suspension, loaded in a 0.25-mm cell, was scanned from 5 to 6.5 μ on a double beam spectrometer equipped with CaF_2 optics. An identical cell containing pyridine was placed in the reference beam for compensation. The standard was scanned between the sample runs to measure absorbance level shifts due to instrumental and cell changes.

The absorbance measured at 5.9 μ was divided by the absorptivity derived from the average of the two absorbance readings of the adjacent standard runs to determine polymaleic acid content.

Four of the samples were examined using the KBr technique of solid-state quantitative analysis, and the results agreed within ±8% of those reported here. Because of poorer reproducibility, the KBr method was discarded in favor of this suspension technique.

Hydrogenation of 5-Methylenebicyclo(2.2.1)-2-heptene (II)–Maleic Anhydride (I) Copolymer

A 51-g sample of Copolymer I-II from Run 6, Table 2, mp 248-271°

(sealed tube), was dissolved in 638 g dry, distilled tetrahydrofuran in a 1410-ml stainless steel autoclave and 5.1 g platinum oxide (Englehard Inc., 84.09%) were added (670 ml volume). The system was purged with N_2, capped, and pressured to 1000 psig with H_2. The temperature immediately rose 5° and the total pressure drop was approximately 255 psi. Heating to 100° gave no further pressure drop.

A blank run using 670 ml tetrahydrofuran and 5.1 g platinum oxide gave a pressure drop of 160 psi. The 95 psi pressure drop due to copolymer present corresponded to 0.12 moles H_2 (0.48 moles H_2/mole copolymer).

The H_2 pressure was relieved, the solution filtered, and the clear filtrate evaporated until the residue reached a constant weight, 42.5 g. This copolymer melted at 211-262° (sealed tube), and the absorbance at 3090 cm^{-1} had decreased from 0.130 to 0.094.

Ammonolysis of 5-Methylenebicyclo(2.2.1)-2-heptene (II)–Maleic Anhydride (I) Copolymer

A 20.4 g sample of copolymer from Run 6, Table 2, was added to 300 ml concentrated ammonium hydroxide. The heterogeneous solution was heated to 72° in 1 hr 40 min, yielding a homogeneous solution. The cooled solution was poured into 200 ml water containing ice and acidified to pH 2. The resulting thick latex-type suspension was centrifuged (basket), yielding a gel. This gel was dissolved in an acetone-water mixture and precipitated by adding a large volume of acetone. The precipitate was centrifuged and the solid dried to constant weight, 7.3 g at 0.1 mm.

The dried polymer did not melt below 360°. It dissolved in aqueous sodium hydroxide, giving a milky and mildly soapy solution. The IR spectrum showed major absorptions at 3.15 and 3.8 μ (acid OH), 5.85 μ (acid carbonyl), 3.0 μ doublet (amide NH_2), and 6.05 μ (amide carbonyl).

Analysis calculated for $C_{12}H_{15}NO_3$: N, 6.34. Found: N, 6.29.

Reaction of Aniline with 5-Methylenebicyclo(2.2.1)-2-heptene and Maleic Anhydride Copolymer

A mixture composed of 20.4 g copolymer from Run 6, Table 2, 9.3 g aniline, and 250 ml pyridine was refluxed 1 hr at 115°, cooled to 30°, added to 250 ml water, and acidified to pH 2. The precipitated polymer was centrifuged and the solid dried at 0.1 mm to constant weight, 28.5 g. The powder was beaten with 400 ml water in a Waring blendor, filtered, and dried to constant weight, 23.5 g

The IR spectrum of this copolymer exhibited absorptions at 3.15 and 3.8 μ (acid OH); 5.85 μ (acid carbonyl); 6.0 and 6.5 μ (secondary amide); and 6.3, 13.2, and 14.5 μ (monosubstituted aromatic ring). Analysis calculated for $C_{18}H_{19}NO_3$: C, 72.7; H, 6.40; N, 4.71. Found: C, 71.84; H, 6.44; N, 4.12.

Viscosity Experiments

Limiting viscosity numbers (intrinsic viscosities) were determined using dilute solutions of copolymers in methyl ethyl ketone. Flow times through a Cannon-Fenske viscometer were determined in a constant temperature bath maintained at 25.00 ± 0.02° using a stop watch which read to 0.01 sec. Collected data was plotted as $(\ln t/t_0)/C$ vs. C, and the resulting curves are shown in Fig. 1.

Copolymerization between Maleimide and 5-Methylenebicyclo(2.2.1)-2-heptene (II)

Maleimide, 11.8 g (0.122 mole), mp 92.0-93.5°, prepared according to the procedure of Snyder et al., [10] was mixed with 30.5 ml xylene, 6.5 g (0.061 mole) II, and 0.015 g (6×10^{-5} mole) dibenzoylperoxide. This mixture was heated to 93° and maintained at 92-93° for 3 hr while stirring under N_2. The reaction mixture was cooled to 30° and filtered by suction. The filter cake was beaten in a Waring blendor with 200 ml methanol, filtered, and dried at 25° (0.08 mm.) to a constant weight of 5.1 g. This copolymer did not melt below 360° and turned brown at 293°.

A sample was used for analyses. The IR spectrum showed characteristic absorptions at 3.10 μ (imide N–H), 5.63 and 5.85 μ (carbonyl), 7.5 μ (amide), and 8.5 μ (carbonyl). These absorptions also occur in maleimide.

Analysis calculated for $C_{12}H_{19}N_3O_6$: C, 60.4; H, 4.82; N, 10.57. Found: C, 56.60; H, 4.83; N, 10.83.

Copolymerization between Bicyclo(2.2.1)-2,5-heptadiene (VII) and Maleic Anhydride (I)

The desired quantity of I was dissolved in xylene at 50° under N_2 and stirred until homogeneous. The desired amounts of VII and dibenzoylperoxide were then added and the mixture was immersed in a water bath maintained at 90°. The mixture was stirred throughout the reaction while maintaining a slow N_2 purge.

After the elapsed time of heating, the heterogeneous mixture was quenched with a xylene solution of N-phenyl-2-naphthylamine, allowed to cool to 25°, and filtered by suction under a N_2 atmosphere.

The filter cake was beaten approximately 60 sec with 250 ml xylene in a Waring blendor, filtered by suction under N_2, and dried to constant weight at ~0.1 mm and 90°. Pertinent data on runs will be found in Table 4. The copolymers were hydrolyzed and the molar ratio I:VII determined by potentiometric titration in aqueous acetone using 0.1 N NaOH.

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