

Free Radical Polymerization and Copolymerization of Bicyclo-(2.2.1)-hepta-(2.5)-diene (Norbornadiene)

JOSEPH PELLON, ROBERT L. KUGEL, RUTH MARCUS, and ROBERT RABINOWITZ, *Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut*

Synopsis

A brief study of the homopolymerization of norbornadiene indicated that pre-gel polymer is limited to product having reduced viscosities below 0.2 dl./g. Pre-gel polymer of 17,000 molecular weight was isolated and characterized: pre-gel polynorbornadiene is soluble in benzene or chloroform, softens at 220–240°C., is thermosetting and shows poor molding characteristics. A cast rod of polynorbornadiene was found to have a heat distortion temperature of 186°C. and a flexural strength of 13,300 psi. Copolymer reactivity ratios of norbornadiene (M_1) determined with vinyl acetate were $r_1 = 1.3$ and $r_2 = 0.8$; with *p*-chlorostyrene, $r_1 \approx 0.01$ and $r_2 \approx 85$. Thermal behavior of several copolymers was determined.

INTRODUCTION

Free radical homopolymerization and copolymerization of norbornadiene was initially disclosed in publications by Kargin, Plate, and Dudnik,¹ and by Kolesnikov and co-workers.² The essential aspects of the free radical polymerization of norbornadiene have been outlined by the recent publications of Graham, Buhle, and Pappas,³ Zutty,⁴ and Wiley et al.⁵ The purpose of the present paper is to present a further description of the homopolymerization, properties, and copolymerization reactivity of norbornadiene.

EXPERIMENTAL

Materials Used

Norbornadiene purchased from Shell Chemical Company was purified by fractional distillation in a Todd apparatus. A glass-helices column of intermediate size was used, and a heart cut isolated at a low take-off to reflux ratio (99:1–20:1). Purified monomer was stored under argon or purified nitrogen and used soon after it was distilled. Storage under an inert atmosphere was believed necessary, since the monomer formed a crystalline, nonpolymeric deposit on exposure to air. Other monomers used in copolymerization studies were purified by standard procedures.

Polymerization Procedures

Except for the runs used to prepare polymer for determination of its properties, all other polymerizations were carried out under carefully deaerated conditions in small polymerization tubes using carefully regulated constant temperature baths. Polymer was isolated as indicated in the scale-up procedure which follows.

Scale-up of Homopolymerization

A 250-ml. three-necked round-bottomed flask equipped with a reflux condenser, gas inlet, and outlet tube, and containing an oval Teflon-covered magnetic stirring bar was purged with nitrogen for 1 hr. A slurry of 0.1804 g. of azobisisobutyronitrile (AIBN, 0.1 mole-%) in 100 g. of norbornadiene was added under nitrogen, and the stirred mixture was purged for several minutes with N₂. Polymerization was carried on over a period of 6 hr. at 70°C.

The polymer was isolated by precipitating in hexane. Purification was achieved by twice dissolving in benzene and precipitating in hexane. The polymer was finally dissolved in benzene, filtered, and freeze-dried; yield 5.7 g.

RESULTS AND DISCUSSION

Homopolymerization

A brief study was made of the effect of varying the initiator, temperature, and initiator concentration on the free radical polymerization of norbornadiene. The results are summarized in Tables I and II.

Conversion after 24 hr. with various radical initiators is given in Table I. The temperature used for the different initiators was chosen so that all initiator half-lives would be of the order of 5 hr. Soft gel (Nos. 3 and 4) could be easily broken-up and extracted by boiling benzene. Hard clear plastic (Nos. 5 and 6) was cured and after several hours in boiling benzene was not swollen.

TABLE I
Free Radical Polymerization of Norbornadiene^a

No.	Initiator	Temp., °C.	Appearance	Con- version, %
1	Thermal	70	Colorless liquid	0
2	Thermal	150	Colorless liquid	Trace
3	Azobisisobutyronitrile	70	Colorless gel	56 ^b
4	Benzoyl peroxide	80	Light-yellow gel	36 ^b
5	<i>tert</i> -Butyl perbenzoate	110	Light-yellow hard solid	—
6	Di- <i>tert</i> -butyl peroxide	130	Colorless hard solid	—

^a Polymerization run in bulk for 24 hr. at 1 mole-% initiator.

^b Represents insoluble polymer isolated after extraction with boiling benzene.

TABLE II
Effect of Reaction Conditions on Polymer Viscosities

Initiator	Initiator concn., mole-%	Temp., °C.	Time, hr.	Con- version, %	Reduced viscosity, dl./g. ^a
Di- <i>tert</i> -butyl peroxide	0.1	130	2	5	0.14
	0.01	130	2	3	0.14
	0.01	120	20	4.6	0.10
	0.01	110	48	3.8	0.15
Azobisisobutyronitrile	0.4	70	3	6.7	0.2
	0.01	70	7	4	0.14
	0.1	60	24	3.2	0.13
	0.01	60	48	1.7	0.14
	0.1	30	792	4	0.19 ^b
Spontaneous ^c	Room temp.		—	0.8	0.11

^a Reduced viscosity in benzene at 0.1%.

^b Reduced viscosity in chloroform.

^c Polymer was isolated from a sample of monomer which had been exposed several times to the air and then allowed to stand at room temperature.

In a search of conditions for obtaining soluble polymers of norbornadiene of maximum molecular weight, reaction temperature and initiator concentration were varied to alter the polymerization rate. Results are given in Table II.




The polymer molecular weights were found not to be sensitive to the rate of polymerization; reduced viscosities all were in the range of 0.1–0.2 dl./g.

Attempts at emulsion polymerization of norbornadiene also gave pre-gel polymers having intrinsic viscosities less than 0.1 dl./g. at low conversions and insoluble polymers at higher conversions.

It was of interest to compare the overall polymerization behavior of norbornadiene to other cyclic olefins. Results given in Table III show that ease of polymerization decreased in the order:



TABLE III
Relative Polymerizability of Cyclic Olefins

Initiator	Temp., °C.	Conversion, % ^a		
				
Azobisisobutyronitrile	70	0	1	Soft gel
<i>tert</i> -Butyl perbenzoate	110	0	2	Cured solid
Di- <i>tert</i> -butyl peroxide	130	0	12	Cured solid

^a Conversion after 24 hr. with 1 mole-% initiator.

Homopolymer Properties

Table IV summarizes the properties of polynorbornadiene isolated at low conversions.

The free radical polymerization of norbornadiene is typified by the formation of soluble low molecular weight polymer at low conversions while higher conversion leads to cross linked polymer.

The essential features of the spectra (infrared and NMR) of the homopolymer prepared in this study are in accord with those recently reported by Wiley et al.⁵ for the radiation-polymerized norbornadiene of 1500 molecular weight. These authors consider the ratio of nortricyclene (A) to norbornylene (B) units in their polymer (I) to be equal to 2/1.

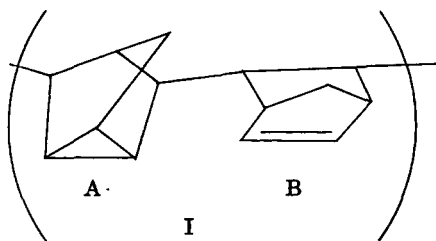


TABLE IV
Properties of Polynorbornadiene Obtained at Low Conversions^a

Appearance	White powder
Conversion, %	6
Solubility	Soluble in benzene, tetrahydrofuran, CHCl ₃ , and CCl ₄
Density, g./cc.	1.033
Crystallinity (x-ray)	Amorphous
Intrinsic viscosity, dl./g. ^b	0.20
Huggins' constant k' ^c	0.06
Molecular weight M_w ^d	17,000
Ratio of unsaturated protons to saturated protons ^e	1/17.5
Infrared ^f	Strong peaks at 710, 800 and 3050 cm. ⁻¹
Thermal behavior on heating	Darkened at 225°C., softened at 238°C.; thermoset
Thermogravimetric analysis ^g	
In air T_i = 130°C.	
T_{10} = 322°C.	
In N ₂ T_{10} = 348°C.	

^a Polymer prepared by polymerization for 6 hr. at 70°C. with 0.1 mole-% azobisisobutyronitrile (see Experimental).

^b In CHCl₃ at 30°C.

^c Calculated from the formula $\eta_{sp}/c = [\eta] + k'[\eta]^2/c$.

^d Light scattering in benzene.

^e Nuclear magnetic resonance in CDCl₃, ratio of area 3.90 τ /7-10 τ .

^f Infrared in KBr pellet.

^g T_i = temperature at which initial weight loss occurs; T_{10} = temperature at which 10% weight loss has occurred; heating rate is 10°C./min.

On the basis of the NMR data, homopolymer prepared in this study was found to have an A/B ratio of 3.6/1.

TABLE V
Mechanical Properties of Cast Polynorbornadiene^a

	Polynorbornadiene	Poly(methyl methacrylate)
Heat distortion temp., °C.	186	76
Impact strength, ft./lb./in. ²	3.5	4.0
Flexural strength, psi	13,300	17,000 ± 600
Flexural modulus, psi	0.38 × 10 ⁶	0.49 × 10 ⁶

^a Rods 6 in. in length were machined and polished to 1/4 in. diameter and used in determining physical properties.

TABLE VI
Determination of Reactivity Ratios for Norbornadiene (M₁)

Comonomer (M ₂)	Molar feed ratio, M ₁ /M ₂ ^a	Adjusted molar feed ratio, M ₁ /M ₂ ^b	Conver- sion, %	Analysis, % carbon	Molar polymer ratio, M ₁ /M ₂	Reactivity ratios ^c	
						r ₁	r ₂
Vinyl acetate	0.2579	0.2550	10.4	64.76	0.3162	1.28	0.82
	0.3767	0.3703	15.4	67.75	0.4752		
	0.4078	0.4030	11.0	68.15	0.4997		
	0.6476	0.6362	13.4	72.46	0.8286		
	1.316	1.311	6.65	77.56	1.4851		
	3.116	3.100	5.9	84.10	3.6983		
	4.832	4.819	4.3	86.71	6.3946		
<i>p</i> -Chloro- styrene	2.0517	2.2212	6.5	69.49	0.0110	0.01	85
	2.7243	2.9890	6.6	69.84	0.0358		
	3.9195	4.4451	6.9	70.08	0.0533		
	5.4045	6.0317	4.9	70.82	0.1097		
	7.4568	8.3371	3.8	70.68	0.0987		

^a Mixtures of 3–5 g. of monomer and about 15 mg. of azobisisobutyronitrile.

^b Average of initial and final monomer ratios.

^c Calculated on the basis of the Fineman-Ross equation.

TABLE VII
Copolymerization of Vinyl Acetate and Norbornadiene^a

AIBN, g. ^b	Time, hr.	Conversion, %	Reduced viscosity, dl./g. ^b
0.0009	48	8.0	0.22
0.0030	20 1/4	8.6	0.22
0.0028	48	Gel	—
0.0028	32	24.5	0.33

^a Monomer feed 2.6 g. vinyl acetate and 1.8 g. norbornadiene.

^b Measured at 0.5% concentration in benzene at 30°C.

TABLE VIII
Scale-Up Copolymerization Results^a

Comonomer (M ₂)	Composition of feed				Time, hr.	Conver- sion, %	Intrinsic viscosity, dl./g. ^b	Poly- mer M ₁ /M ₂	Thermal behavior			
	M ₁ , g.	M ₂ , g.	AIBN, g.	Molar ratio M ₁ /M ₂					Softening temp., °C. ^c	Flow temp., °C. ^c	T ₁₀ , °C. ^d	
Vinyl acetate	23.05	33.6	0.039	0.641	16	12.2	0.26	0.7195	70-100	110-160	Air	328
Vinyl acetate	97.20	29.16	0.360	3.115	25.5	11.2	0.15	3.5106	80-135	240 ^e	300	343
Methyl methacrylate	86.99	21.01	0.15	4.498	5	7.7	0.37	0.1191	80	140	335	335
Styrene	86.88	13.19	0.894 ^f	7.4428	106 ^f	7.6	0.12	No anal- ysis	100-110	115-135	350	365
Acrylonitrile	28.6 ^g	31.7	0.24	0.520	11.25	—	0.19 ^h	0.467	100	135-160	383	384

^a M₁ = norbornadiene, temperature = 60°C.

^b In benzene at 30°C.

^c Using a Fisher John's melting point apparatus.

^d Temperature at which 10% weight loss occurs when a sample is heated at 10°C./min.

^e Never free flowing.

^f 0.385 g. added at 0 hr.; 0.214 g. added at 34 hr.; 0.295 g. added at 87 hr.

^g Run in 75 ml. of butyrolactone.

^h In acetone.

Properties of Polynorbornadiene Casting

Polynorbornadiene, described in Table IV, could not be molded to give test specimens suitable for determining physical properties. Standard procedures for preparing test specimens by cast polymerization proved inapplicable since adequate curing was obtained only at temperatures above the boiling point of the monomer (90–160°C.). However, rods of the polymer were successfully cast in sealed glass tubes using an aluminum liner to prevent crazing. Since the rods were not standard test specimens it was necessary to compare physical properties with those of a known plastic in the same form. Table V gives a comparison of the physical properties of cast polynorbornadiene with poly(methyl methacrylate).

Copolymerization

Reactivity ratios of norbornadiene with vinyl acetate and *p*-chlorostyrene were determined; data are presented in Table VI.

The reactivity ratios determined in this study and those given by Zutty⁴ clearly define the reactivity of norbornadiene to be of a low order.

Copolymer Properties

Copolymerization of norbornadiene was generally in accord with behavior expected on the basis of data on the homopolymerization. In the copolymerization of norbornadiene with vinyl acetate, polymer viscosities were independent of initiator concentration but were directly related to conversion. The viscosity increased as the gel point was approached. In one of the examples tabulated in Table VII, copolymerization was carried to 24.5% conversion without gelation. It was observed, as expected, that as the percentage of norbornadiene in the monomer mixture decreased, the conversion before gelation increased.

As indicated by data given in Table VIII, the solubility and thermal behavior of the copolymers of norbornadiene were in most cases "averages" of the monomer pairs. A copolymer of vinyl acetate and norbornadiene containing 3 moles of norbornadiene to 10 of vinyl acetate started to soften and could be pressed to yield transparent spots at 50°C. Another copolymer containing 6.5 moles of norbornadiene to 1 mole of vinyl acetate did not soften with pressing until 230°C. and never melted. At 280°C. it became yellow and was later found to be insoluble in benzene.

Structural infrared analysis on polynorbornadiene was carried out by Dr. M. Tobin and Mr. N. Colthup, and nuclear magnetic resonance studies by Dr. J. Lancaster. We also acknowledge the contribution by Mr. W. G. Deichert who carried out several preliminary polymerization experiments.

References

1. Kargin, V. A., N. A. Plate, and L. A. Dudnik, *Vyskomol. Soedin.*, **1**, 420 (1959).
2. Kolesnikov, G. S., et al., *Vysokomol. Soedin.*, **2**, 451 (1960).
3. Graham, P. J., E. L. Buhle, and N. Pappas, *J. Org. Chem.*, **26**, 4658 (1961).
4. Zutty, N. L., *J. Polymer Sci.*, **A1**, 2231 (1963).
5. Wiley, R. H., W. H. Rivera, T. H. Crawford, and N. F. Bray, *J. Polymer Sci.*, **61**, 172 (1962).

Résumé

Une étude brève de l'homopolymérisation du norbornadiène indique qu'un polymère était obtenu présentant une viscosité réduite, inférieure à 0.2 dl/g. Un polymère pré-gel d'un poids moléculaire de 17.000 fut isolé et ses caractéristiques étudiées: le polynorbornadiène est soluble dans le benzène, ou le chloroforme, ramollit à 220–240°C, est thermostable et présente de pauvres caractéristiques de moulage. On trouve qu'une barre coulée de polynorbornadiène présente une température de distorsion à la chaleur de 186°C et une force de rupture à la flexion de 13.300 livres/pouce². Les paramètres de réactivité de la copolymérisation du norbornadiène (M_1) avec l'acétate de vinyle sont $r_1 = 1.3$ et $r_2 = 0.8$; avec le *p*-chlorostyrène on trouve $r_1 \approx 0.01$ et $r_2 \approx 85$. On a étudié le comportement thermique de plusieurs copolymères.

Zusammenfassung

Eine kurze Untersuchung der Homopolymerisation von Norbornadien zeigte, dass Prägelpolymeres auf ein Produkt bei reduzierten Viskositäten unter 0,2 dl/g beschränkt ist. Prägelpolymeres mit dem Molekulargewicht 17.000 wurde isoliert und charakterisiert: Prägelpolynorbornadien ist in Benzol oder Chloroform löslich, erweicht bei 220–240°, ist wärmehärtbar und zeigt schlechte Spritzgusscharakteristik. Ein Gussstab aus Polynorbornadien besitzt eine Wärmebeständigkeitsgrenze von 186°C und eine Biegebeständigkeitsgrenze von 186°C und eine Biegefestigkeit von 13.300 lb/in². Die mit Vinylacetate bestimmten Copolymerreaktivitätsverhältnisse von Norbornadien (M_1) waren $r_1 = 1,3$ und $r_2 = 0,8$, mit *p*-Chlorstyrol $r_1 \approx 0,01$ und $r_2 \approx 85$. Das thermische Verhalten einiger Copolymerer wurde bestimmt.

Received September 20, 1963

Revised November 25, 1963