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Donor-Acceptor Complexes in Copolymerization. LXIII. Alternating Diene-Dienophile Copolymers. 15. Copolymerization of Cyclopentadiene and the Isomeric N-Phenyl-5-norbornene-2,3-dicarboximides with N-Phenylmaleimide

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ABSTRACT

The copolymerization of cyclopentadiene (CPD) and N-phenylmaleimide (NPMI) at 80-195°C, in the presence of a radical catalyst having a short half-life at the reaction temperature and less than 25% solvent, yields a 1:2 CPD-NPMI copolymer (DP 2-3) which is identical (IR, NMR) to the endo 1:1 copolymer (DP 18) obtained under the same conditions from the copolymerization of the endo CPD-NPMI Diels-Alder adduct and NPMI. The exo CPD-NPMI adduct copolymerizes with NPMI under the same conditions to yield an exo 1:1 copolymer (DP 8). Under the same conditions the homopolymerization of the endo and exo CPD-NPMI adducts is effected in the melt at temperatures up to 260°C and in solution at 120-155°C. The homopolymers (DP 3-7) prepared below 210°C retain the configuration of the adducts while the homopolymers prepared at 260°C from either isomer contain both endo and exo configurations due to isomerization. The participation of excited species is suggested by the requirement for high-speed decomposition of radical catalysts to effect homopolymerization and copolymerizations.

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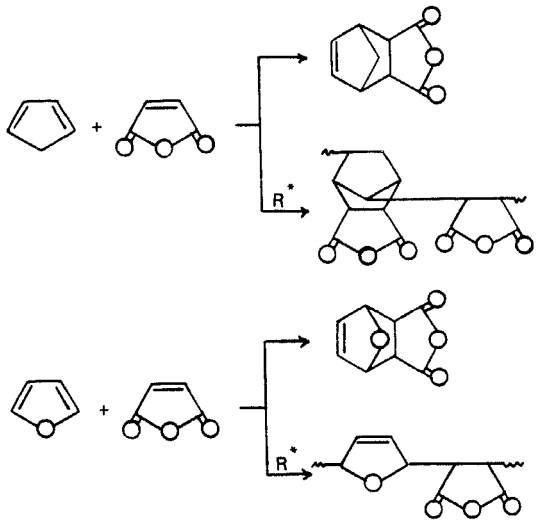
INTRODUCTION

The uncatalyzed reactions of maleic anhydride (MAH) with cyclopentadiene (CPD) and with furan (F) yield the equimolar cyclic Diels-Alder adducts. However, in the presence of a free radical precursor which has a short half-life at reaction temperature, diene-dienophile copolymerizations occur to yield a saturated 1:2 CPD-MAH copolymer [1, 2] and an unsaturated 1:1 F-MAH copolymer [2-4], respectively.



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The uncatalyzed reaction of CPD with N-phenylmaleimide (NPMI) yields the equimolar, cyclic endo Diels-Alder adduct, analogous to the uncatalyzed CPD-MAH reaction. The present investigation was undertaken to determine the course of the catalyzed CPD-NPMI reaction as well as that of the homopolymerization of the isomeric endo and exo CPD-NPMI Diels-Alder adducts and their copolymerization with NPMI.

EXPERIMENTAL

Materials

Cyclopentadiene (CPD) was prepared by the thermal cracking of dicyclopentadiene at 180°C and was either used immediately or freshly distilled before use. N-Phenylmaleimide (NPMI), prepared by the reaction of aniline with maleic anhydride (MAH) in benzene

solution, followed by heating the precipitated product in glacial acetic acid, was recrystallized from a benzene-hexane mixture. Recrystallized CPD-MAH Diels-Alder adduct, endo-cis-5-norbornene-2,3-dicarboxylic anhydride, mp 165°C, was maintained at 220°C for 4 h to yield a crude mixture of endo and exo anhydrides, mp 101°C. The mixture was recrystallized three times from benzene to isolate the exo isomer, mp 141°C. The endo and exo CPD-NPMI Diels-Alder adducts, cis-N-phenyl-5-norbornene-2,3-dicarboximides, mp 144 and 197°C, respectively, were prepared by reaction of the endo and exo CPD-MAH adducts with aniline.

Catalysts having half-lives of less than 2 h at reaction temperature included t-butyl peroxypivalate (tBPP) (75% in mineral spirits) for reactions at 80-90°C, benzoyl peroxide (BP) for reactions at 120°C, t-butyl peroxyacetate (tBPA) (75% in benzene or mineral spirits) and t-butyl perbenzoate (tBPB) for reactions at 150-170°C, and 70% t-butyl hydroperoxide (tBHP-70) (containing 20% di-t-butyl peroxide) for reactions at 195-205°C.

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Uncatalyzed Reaction of CPD and NPMI

A test tube was charged with 0.32 g NPMI and 0.5 mL chlorobenzene (CB) and, after nitrogen flushing, was sealed with a rubber serum cap and immersed in a constant temperature bath at 150°C. The addition of 0.12 g CPD to the NPMI solution was carried out in 4 equal portions over a 10-min period by means of a hypodermic needle injected through the cap of the tube. After an additional 40 min at 150°C, a needle was injected into the cap and unreacted CPD was vented. The tube was removed from the bath and permitted to cool to 25°C. After 2 d the white crystals which separated from the solution and those precipitated by the addition of hexane to the filtrate were dried in vacuo at 25°C. The yield of endo-cis-N-phenyl-5-norbornene-2,3-dicarboximide, mp 143-144°C, was 0.40 g (92%).

Copolymerization of CPD and NPMI

The catalyzed reactions between CPD and NPMI were carried out at 80-205°C by either (a) addition of a solution of catalyst in CPD to molten NPMI, (b) addition of a solution of catalyst in CPD to a preheated solution of NPMI in CB or o-dichlorobenzene (DCB), or (c) simultaneous addition of a solution of catalyst in CPD and a solution of NPMI in CB or DCB to a preheated reaction tube. The addition of reactant solutions was made in 4 portions over a 20-min period by means of needles injected through the cap of the tube which was immersed in a constant temperature bath. The reaction tube was kept in the bath for 40 min after completion of the addition (total time at temperature 1 h). The reaction mixture was cooled and poured into methanol to precipitate the polymer. The latter was purified by

solution in chloroform and precipitation by addition of the solution to methanol.

Copolymerization of CPD-NPMI Adducts and NPMI

The catalyzed copolymerizations of the endo and exo CPD-NPMI Diels-Alder adducts with NPMI were carried out either by adding the catalyst to the preheated solution of the adduct and NPMI in cyclohexanone (CHO) at 90°C or by the simultaneous addition of a solution of tBPP and the adduct in CB and a solution of NPMI in CB to a preheated reaction tube at 80°C, over a 20-min period, followed by 40 min at temperature. The copolymer was isolated and repurified by solution in chloroform and precipitation in methanol.

Homopolymerization of CPD-NPMI Adducts

The catalyzed homopolymerization of the endo and exo CPD-NPMI Diels-Alder adducts was carried out by the addition of the catalyst in 4 portions over 20 min to the molten adduct at 150-260°C or to a solution of the adduct in 1,2-dichloroethane (DCE) or CB at 85-170°C, followed by an additional 10 or 40 min at temperature. The product was isolated by solution in chloroform and precipitation in methanol and purified either in the same manner (exo adduct) or by solution in acetone and precipitation in methanol (endo adduct).

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Characterization

The infrared spectra were obtained from thin films cast on NaCl plates from acetone or chloroform solutions of the polymers, using a Perkin-Elmer Model 137 NaCl Spectrophotometer. The ^{1}H-NMR spectra were obtained from $CDCl_3$ solutions of the polymers with tetramethylsilane as internal standard using a Varian 60 MHz NMR spectrometer.

Molecular weights were determined by vapor pressure osmometry in chloroform and from the NMR spectra. Elemental analyses were carried out by PCR Inc. and Galbraith Laboratories Inc.

RESULTS

Copolymerization of CPD and NPMI

The uncatalyzed reaction of CPD and NPMI at 25-150°C resulted in the formation of the endo CPD-NPMI adduct. The presence of a radical catalyst had little or no effect on the course of the reaction,

i.e., adduct formation, when the catalyst was used under conditions which are normally effective in conventional radical-initiated polymerization, i.e., at temperatures where the catalyst half-life is 3-10 h and with solvent concentrations of more than 25% of the volume of the reaction mixture.

When the catalyst was used at a temperature where it has a short half-life and the solvent concentration was limited to that amount which was necessary to form a homogeneous reaction mixture at that temperature, the reaction course changed from adduct formation to polymerization. The use of radical catalysts at temperatures where the half-life is less than 2 h has previously been shown to be effective in the homopolymerizations of MAH [5], norbornene [6, 7], the CPD-MAH adducts endo- and exo-cis-5-norbornene-2,3-dicarboxylic anhydrides [2, 8, 9], and the CPD-NPMI adducts endo- and exo-N-phenyl-5-norbornene-2,3-dicarboximides [10] as well as the copolymerizations of conjugated dienes and MAH [1, 2, 11-13].

The addition of a solution of catalyst in CPD to molten NPMI at 155 or 205°C resulted in the formation of the chloroform-soluble homopolymer of NPMI, i.e., poly(N-phenylmaleimide), identified by elemental analysis and ^{1}H-NMR spectroscopy. The product obtained at 205°C was acetone-insoluble while the product obtained at 155°C consisted of a mixture of acetone-soluble and acetone-insoluble fractions. Both fractions had elemental analyses and NMR spectra in agreement with that expected for the homopolymer. The latter, prepared by homopolymerization of NPMI in the presence of tBPP at 90°C or tBHP-70 at 205°C, was chloroform-soluble and acetone-insoluble. The acetone-soluble fraction obtained at 155°C may have contained some copolymerized CPD, possibly in the form of the copolymerized CPD-NPMI Diels-Alder adduct.

The addition of a solution of tBPP in CPD to a preheated solution of NPMI in CB at 85°C gave a chloroform-soluble, acetone-soluble saturated 1:2 CPD-NPMI copolymer, identified by elemental analysis and ^{1}H-NMR. The same 1:2 CPD-NMPI copolymers were also obtained by the simultaneous addition of a solution of catalyst, i.e., tBPP, tBPA, or tBHP, in CPD and a solution of NPMI in CB or DCB to a preheated reaction tube maintained at 80-195°C (Table 1). The infrared spectra of the copolymers obtained at 90, 155, and 195°C are identical and superimposable (Fig. 1), and differ only slightly, in the 3.3-3.5 μm region from the spectrum of the NPMI homopolymer.

The NMR spectra of the copolymers indicated the presence of catalyst moieties, i.e., t-butoxy groups. The molecular weight of the copolymer obtained at 90°C was 1374 while that of the copolymer obtained at 195°C was 960, representing trimeric and dimeric units, respectively, i.e.,

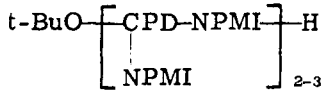

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TABLE 1. Copolymerization of Cyclopentadiene (CPD) with N-Phenylmaleimide (NPMI)

CPD (mmol)	NPMI (mmol)	Solvent (mL)	Catalyst (mmol)	Temperature (°C)	Method[a]	Yield (%)[b]	Product
12.1	8.7	-	tBPA 0.7	155	A	73.3	P(NPMI)[c]
20	20	-	tBHP-70 4.0	205	A	81.2	
12.1	8.7	CB 4	tBPP 1.0	85	B	30.7	
14.5	11.6	CB 6	tBPP 1.0	80	C	15.5	
10	10	CB 8	tBPP 1.0	90	C	19.9[e]	
12.1	8.7	CB 4	tBPA 0.7	155	C	50.3	1:2 copolymer[d]
15.2	8.7	CB 4	tBPA 0.8	155	C	49.7	
9.4	7.5	CB 6	tBPA 0.8	155	C	42.6	
10	10	DCB 9	tBHP-70 2.0	195	C	48.5[f]	
1.82	1.85	CB 0.5	-	150	D	92.0	1:1 adduct[g]

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[a]Methods: A, solution of catalyst in CPD added to molten NPMI.
B, solution of catalyst in CPD added to preheated solution of NPMI in CB.
C, solution of catalyst in CPD and solution of NPMI in CB or DCB added simultaneously to preheated reaction tube.
D, CPD added to solution of NPMI in CB at temperature.

[b]Based on charge for P(NPMI), 1:2 CPD-NPMI composition for copolymer and 1:1 CPD-NPMI composition for adduct.

[c]Mixture of acetone-soluble and acetone-insoluble fractions identified as P(NPMI) by ^{1}H NMR and elemental analysis.

Calcd for $C_{10}H_7O_2N$: C,	69.36; H,	4.05; N,	8.09
Anal. soluble fraction:	69.93	4.71	7.56
insoluble fraction:	69.15	4.33	7.46

[d]Identified as 1:2 copolymer by ^{1}H NMR and elemental analysis.

Calcd for $C_{25}H_{20}O_4N_2$: C,	72.82; H	4.85; N,	6.80
Anal:	72.43	5.32	6.30

[e]Mp 255-256°C; molecular weight 1374.
[f]Mp 257-258°C; molecular weight 960.
[g]endo CPD-NPMI Diels-Alder adduct, mp 143-144°C.

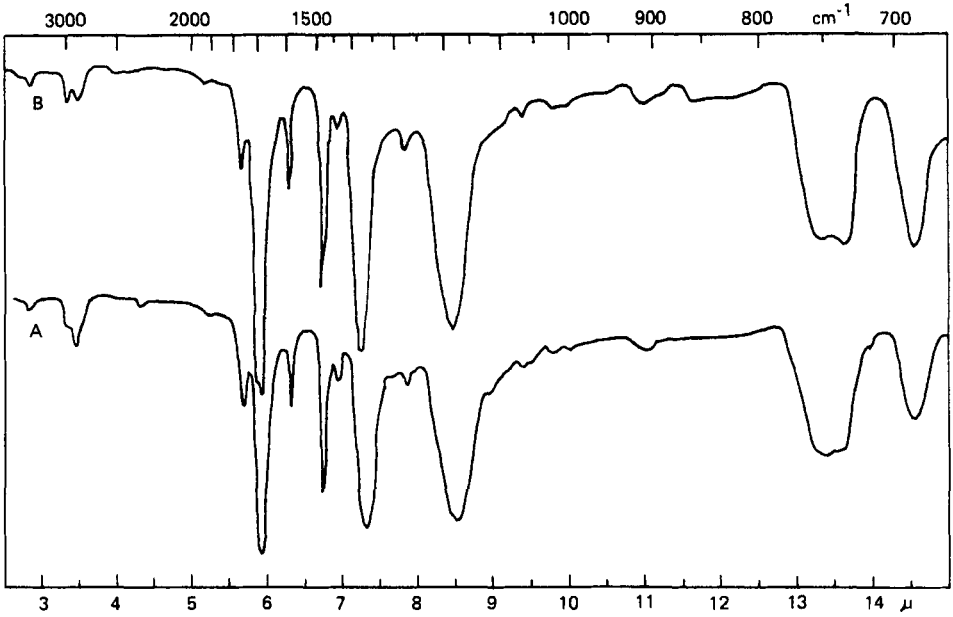

FIG. 1. Infrared spectra: (A) 1:2 CPD-NPMI copolymer from copolymerization of CPD and NPMI at 155° C with tBPA; (B) P(NPMI) from homopolymerization of NPMI at 90°C with tBPP.

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Copolymerization of N-Phenyl-5-norbornene-2,3-dicarboximides and NPMI

The radical catalyzed copolymerization of the endo and exo CPD-NPMI Diels-Alder adducts with NPMI was carried out at 80-90°C by the addition of tBPP to a preheated cyclohexanone (CHO) solution of the adduct and NPMI or by the simultaneous addition of a solution of the adduct and tBPP in CB and a solution of NPMI in CB to a preheated reaction tube. The crude products, precipitated from the reaction mixture with methanol, were purified by solution in chloroform and reprecipitation with methanol (Table 2).

The endo adduct-NPMI copolymer had an equimolar composition and was soluble in acetone, while the equimolar exo adduct-NPMI copolymer was insoluble in acetone. The infrared spectra of the endo CPD-NPMI adduct-NPMI copolymer and the 1:2 CPD-NPMI copolymers prepared by the copolymerization of CPD and NPMI are essentially identical, while the spectrum of the exo CPD-NPMI adduct-NPMI copolymer differs from the others by the presence of a peak at 790-820 cm^{-1} (Fig. 2).

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TABLE 2. Copolymerization of Isomeric N-Phenyl-5-norbornene-2,3-dicarboximides with N-Phenylmaleimide (NPMI)

Adduct	(mmol)	NPMI (mmol)	Solvent (mL)	tBPP (mmol)	Temperature (°C)	Yield (%)	N Analysis (wt%)[c]	Acetone solubility
Endo	5	5	CHO 2	0.52[a]	90	72.0[d]	7.00	Soluble
	5	5	CB 10	1.03[b]	80	55.6	7.17	Soluble
Exo	5	5	CHO 5	0.52[a]	90	89.4[e]	6.55	Insoluble

[a]tBPP added in 4 portions over 20 min to preheated solution of adduct and NPMI in CHO, followed by an additional 40 min at 90°C.

[b]Solution of tBPP and adduct in 5 mL CB and solution of NPMI in 5 mL CB added simultaneously to preheated reaction tube at 80°C over 20 min, followed by 40 min at 80°C.

[c]Calculated for 1:1 copolymer $C_{25}H_{20}O_4N_2$: N, 6.80.

[d]Mp 265-268°C; molecular weight 7508.

[e]Mp 286-288°C; molecular weight 3432.

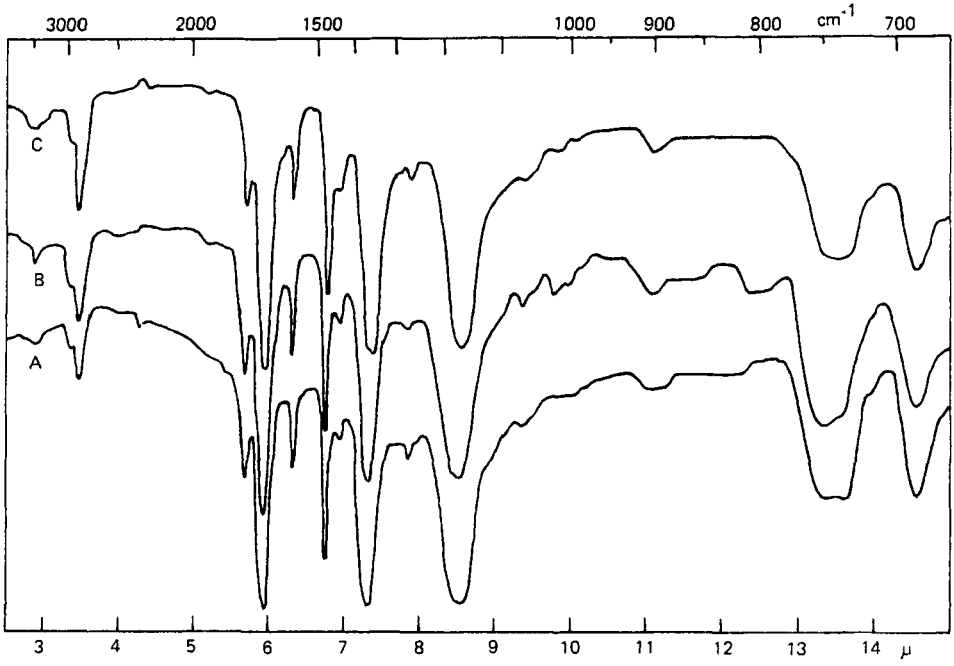

FIG. 2. Infrared spectra of copolymers prepared at 90°C with tBPP: (A) endo CPD-NPMI adduct-NPMI copolymer; (B) exo CPD-NPMI adduct-NPMI copolymer; (C) 1:2 CPD-NPMI copolymer from CPD and NPMI.

The ^{1}H-NMR spectra of the isomeric CPD-NPMI adduct-NPMI copolymers indicate the presence of catalyst residues and the absence of unsaturation and are similar to the spectra of the 1:2 CPD-NPMI copolymers. The spectra are very broad and unresolved. However, a peak at 6.8τ, present in the spectrum of the homopolymer of the endo CPD-NPMI adduct (Fig. 3A), is also present in the spectrum of the copolymer of the endo adduct and NPMI (Fig. 3B). This peak is absent from the spectra of the homopolymer of the exo CPD-NPMI adduct and the copolymer of the exo adduct and NPMI (Fig. 4).

The broad NMR spectra of the 1:2 CPD-NPMI copolymers (Fig. 3C) resemble that of the endo adduct-NPMI copolymer and contain the characteristic peak at 6.8τ (Fig. 3B). This suggests that the 1:2 CPD-NPMI copolymer prepared by copolymerization of CPD and NPMI has the same structure as the 1:2 CPD-NPMI copolymer prepared by copolymerization of the endo CPD-NPMI adduct and NPMI. This is consistent with the acetone solubility of the copolymers prepared by the copolymerization of NPMI with either CPD or the endo CPD-NPMI adduct in contrast with the acetone insolubility of the exo CPD-NPMI adduct-NPMI copolymer.

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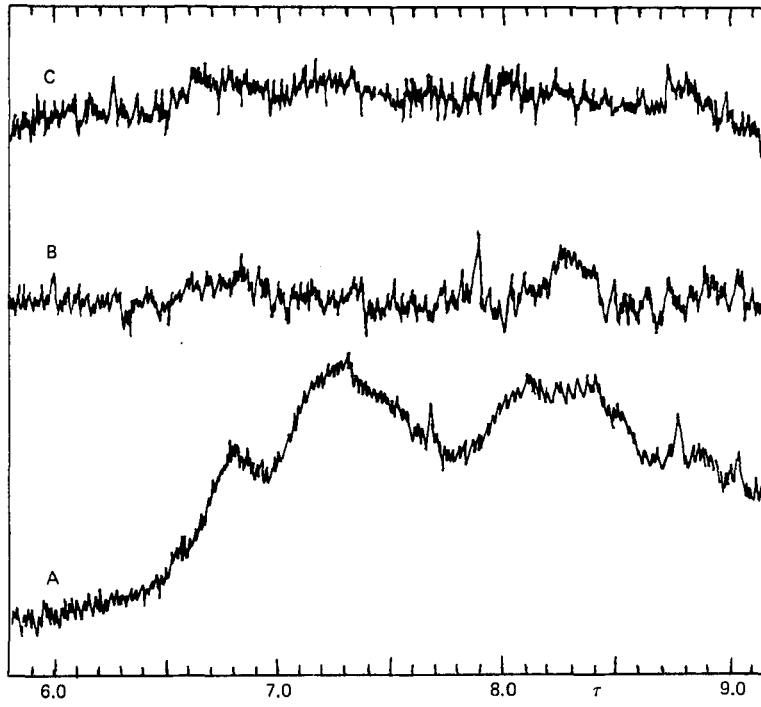
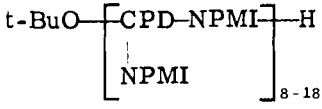


FIG. 3. 60 MHz ^{1}H-NMR spectra: (A) endo CPD-NPMI adduct homopolymer prepared at 120°C with tBPA; (B) endo CPD-NPMI adduct-NPMI copolymer prepared at 80°C with tBPP; (C) 1:2 CPD-NPMI copolymer prepared from CPD and NPMI at 155°C with tBPA.

The molecular weight of the copolymer obtained from the exo adduct-NPMI copolymerization at 90°C was 3432 while that of the copolymer obtained from endo adduct-NPMI copolymerization at 90°C was 7508, representing copolymers containing 8 and 18 (CPD-NPMI)-NPMI units, respectively, in addition to the catalyst moiety:



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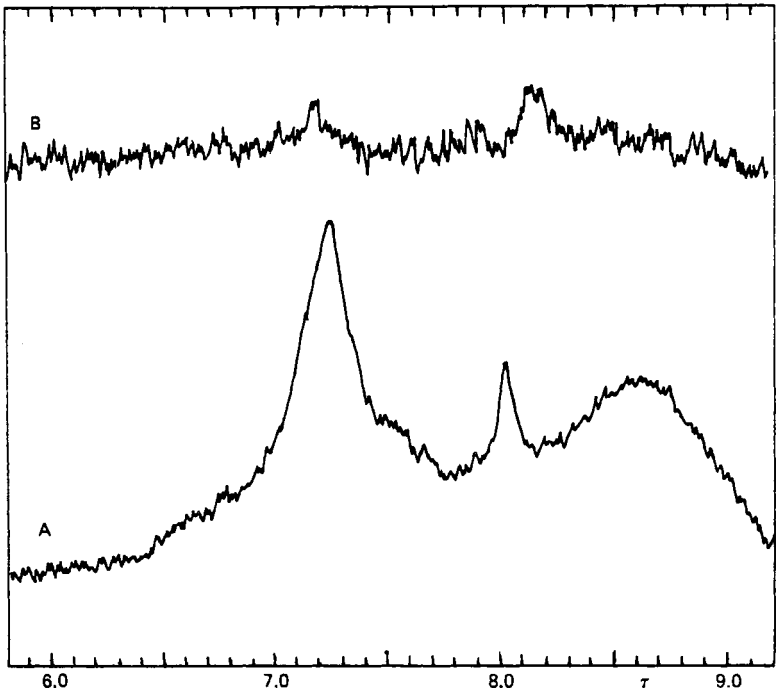

FIG. 4. 60 MHz ^{1}H-NMR spectra: (A) exo CPD-NPMI adduct homopolymer prepared at 155°C with tBPA; (B) exo CPD-NPMI adduct-NPMI copolymer prepared at 90°C with tBPP.

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Homopolymerization of endo and exo N-Phenyl-5-norbornene-2,3-dicarboximides

The homopolymerization of the endo CPD-NPMI Diels-Alder adduct, mp 144°C, was effected in the melt at temperatures ranging from 150 to 260°C by the addition of radical catalysts having short half-lives at the reaction temperature [14]. The endo adduct was also polymerized by the addition of radical catalysts to a solution of the adduct in 1,2-dichloroethane (DCE) at 85°C or in CB at 120 and 150°C (Table 3).

The homopolymerization of the exo CPD-NPMI Diels-Alder adduct, mp 197°C, was also effected in the melt at 260°C and in CB solution at 120-155°C by the addition of radical catalysts with short half-lives. However, the exo adduct failed to undergo polymerization at 85°C in DCE in the presence of tBPP, although the endo adduct did polymerize under these conditions, albeit in low yield.

Although both endo and exo adducts were homopolymerized at 120°C

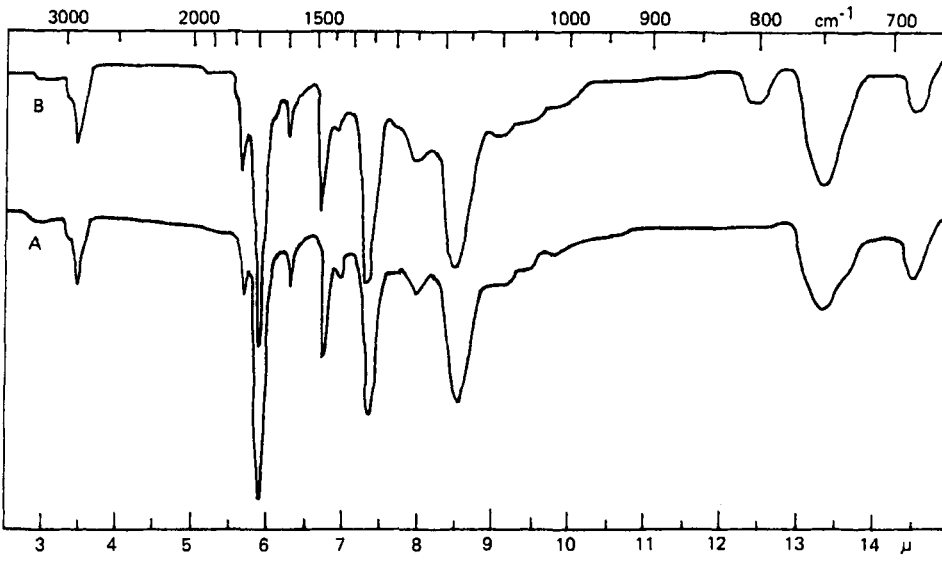

FIG. 5. Infrared spectra of CPD-NPMI adduct homopolymers prepared at 150°C with tBPB: (A) endo adduct homopolymer; (B) exo adduct homopolymer.

in CB by the addition of tBPA in benzene solution, the addition of tBPA in mineral spirits gave a lower yield of the endo adduct homopolymer and failed to promote the polymerization of the exo adduct.

Elemental analysis and ^{1}H-NMR confirmed the equimolar composition of the CPD-NPMI adduct homopolymers, irrespective of polymerization temperature under the conditions studied. The infrared spectra of the endo and exo adduct homopolymers are essentially identical and differ only by the presence of a peak at 790-810 cm^{-1} in the spectrum of the exo adduct homopolymer (Fig. 5). This same peak also differentiates the infrared spectrum of the exo CPD-NPMI adduct-NPMI copolymer from the spectrum of the endo adduct-NPMI copolymer (Fig. 2).

The ^{1}H-NMR spectra of the endo adduct homopolymers prepared at or below 210°C contain a peak centered at 6.8 τ as well as broad peaks at 7.0-7.7 and 7.8-8.6 τ (Fig. 3A). The ^{1}H-NMR spectra of the exo adduct homopolymers prepared below 200°C contain a narrow peak at 7.0-7.4 τ, centered at 7.25 τ, and a broader peak at 8.3-8.9 τ (Fig. 4A). The peak at 6.8 τ, which is present in the spectrum of the endo adduct homopolymer, is absent from the spectrum of the exo adduct homopolymer. Both spectra have the peaks of aromatic hydrogens at 2.4-3.0 τ. Neither spectrum contains peaks at about 4.0 τ, attributable to vinyl hydrogens, indicating the absence of unsaturation.

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TABLE 3. Homopolymerization of endo and exo N-Phenyl-5-norbornene-2,3-dicarboximides[a]

Isomer	(mmol)	Solvent (mL)	Catalyst	(mmol)	(mol%)	Temperature (°C)	Yield (%)	Mp (°C)
Endo	33.5	DCE 10	tBPP	3.7	11.0	85	9	262-264
	8.4	CB 3	tBPA	1.1[b]	13.1	120	16	275-282
	8.4	CB 3	tBPA	1.1[c]	13.1	120	60[d]	265-280
	2.4	CB 2	tBPB	1.3	54.2	150	53[e]	258-260
	8.4	-	tBHP-70	1.3	15.5	150	0	•
	8.4	-	tBPB	1.1	13.1	150	20	265-280
	8.4	-	tBHP-70	1.3	15.5	210	20	265-275
	8.4	-	tBHP-70	1.3	15.5	260	50	265-280
Exo	18.5	DCE 16	tBPP	1.8	9.7	85	0	

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8.4	CB 3	tBPA	1.1[b]	13.1	120	0	
8.4	CB 3	tBPA	1.1[c]	13.1	120	46	240-245
4.2	CB 3	tBPB	0.5	11.9	150	25[f]	263-267
4.2	CB 3	tBPB	2.0	47.6	150	26[g]	253-255
8.4	CB 3	tBPA	1.1[c]	13.1	155	60	250-255
8.4	-	tBHP-90	1.8	21.4	260	30	

[a]Catalyst added in 4 portions to adduct solution at 85-155°C or to molten adduct at 150-260°C over 20 min period, followed by 40 min at temperature.
[b]tBPA (75% in mineral spirits) added over 20 min period, followed by 10 min at 120°C.
[c]tBPA (75% in benzene) added over 20 min period, followed by 40 min at temperature.
[d]Molecular weight 1645 (NMR).
[e]Molecular weight 632 (vpo, $CHCl_3$).
[f]Molecular weight 869 (vpo, $CHCl_3$).
[g]Molecular weight 578 (vpo, $CHCl_3$).

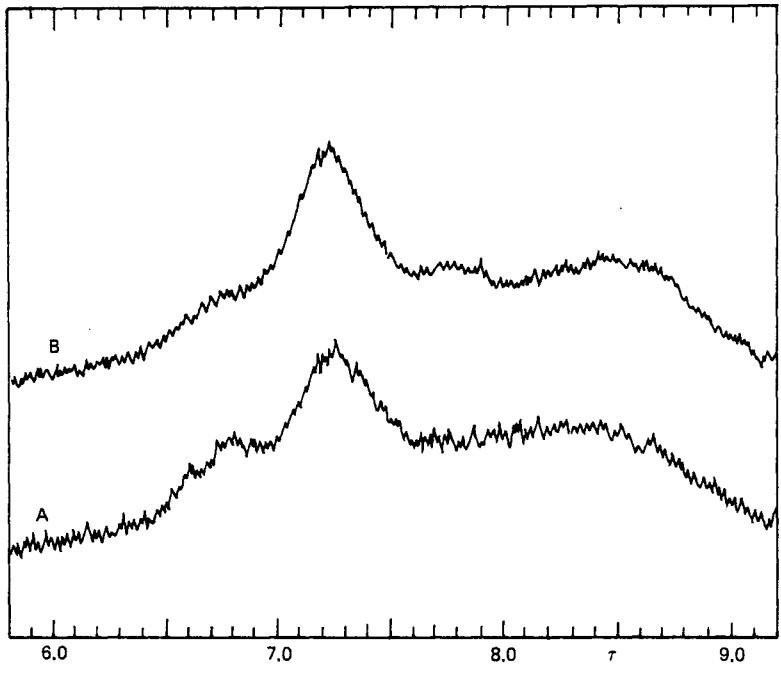

FIG. 6. 60 MHz ^{1}NMR spectra of CPD-NPMI adduct homopolymers prepared at 260°C: (A) exo adduct homopolymer; (B) endo adduct homopolymer.

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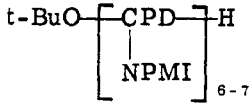
The ^{1}H-NMR spectra of the homopolymers obtained from the endo and exo adducts at 260°C are similar to each other and contain peaks arising from both endo and exo structures (Fig. 6), suggesting that the adducts have undergone endo-exo isomerization during polymerization at 260°C.

Although no isomerization of the endo and exo adducts is detectible by infrared analysis after 5 h at 170°C, a 40/60 endo/exo mixture is obtained after heating either isomer for 30 min at 260°C [14]. Isomerization is reported to occur to some extent at a temperature as low as 200°C [15, 16]. Thus the homopolymers prepared from either isomer at 260°C possess the same structural units and characteristics.

The molecular weight of the homopolymer prepared from the endo CPD-NPMI adduct in CB at 120°C with 13 mol% tBPA in benzene was 1645, as calculated from the NMR spectrum, corresponding to a homopolymer with one catalyst moiety and 6-7 monomer units, i.e.,



The molecular weight of the homopolymer prepared from the exo adduct in CB at 150°C with 12 mol% tBPB was 869 (vapor pressure osmometry in $CHCl_3$), corresponding to a homopolymer with one t-butoxy group and 4 monomer units. Homopolymers prepared from the endo and exo adducts in CB at 150°C with 50 mol% tBPB were trimeric.

DISCUSSION

Infrared analysis indicates no detectible endo-exo isomerization of the CPD-NPMI adducts at temperatures below 170°C. However, some isomerization apparently takes place at 200°C [15, 16]. The endo isomer is the kinetically more favorable isomer while the exo isomer is thermodynamically more favorable [17]. Nevertheless, the endo adduct is the exclusive product when CPD and NPMI undergo the Diels-Alder reaction at 150°C (Table 1).

The preference for endo adduct formation is presumably responsible for the endo structure of the adduct moiety in the 1:2 CPD-NPMI oligomers prepared from the monomers at temperatures ranging from 80 to 195°C in the presence of radical catalysts.

The products presumably arise from the excited state charge transfer complex rather than from the ground state complex from which it arises and which is responsible for the cycloaddition reaction leading to adduct formation. The participation of the excited state complex in the formation of alternating copolymers and of the ground state complex in the formation of cycloadducts has previously been demonstrated in the reactions of acyclic conjugated dienes such as butadiene, isoprene, and piperylene with MAH [12, 13, 18] and with acrylonitrile in the presence of complexing agents such as organoaluminum halides [18, 19]. Excitation of ground state complexes in the presence of species generated from a peroxygen compound under conditions where the latter is undergoing rapid decomposition has been proposed in the polymerization of MAH [5], norbornene [6, 7], and the CPD-MAH Diels-Alder adducts [2, 8, 9], as well as the copolymerization of conjugated dienes and MAH [1, 2, 11-13, 18].

The low molecular weight of the 1:2 CPD-NPMI products from the copolymerization of CPD and NPMI, i.e., 960-1374, corresponding to dimers and trimers, is of the same order of magnitude as the low molecular weight of the 1:2 CPD-MAH products from the copolymerization of CPD and MAH, i.e., 530-1000, corresponding to dimers and tetramers [2]. In both cases the low molecular weight of the products may be due to the quenching action of CPD. Alternatively, the short half-life of the excited monomers, i.e., NPMI* or MAH*, or the exciplexes, i.e., $CPD^{+}\cdot NPMI$ or $CPD^{+}\cdot MAH$, may reduce the concentration of excited species, which are the polymerizable "monomers" and lead to oligomeric products.

Analogous to the formation of the saturated 1:2 CPD-MAH copolymers

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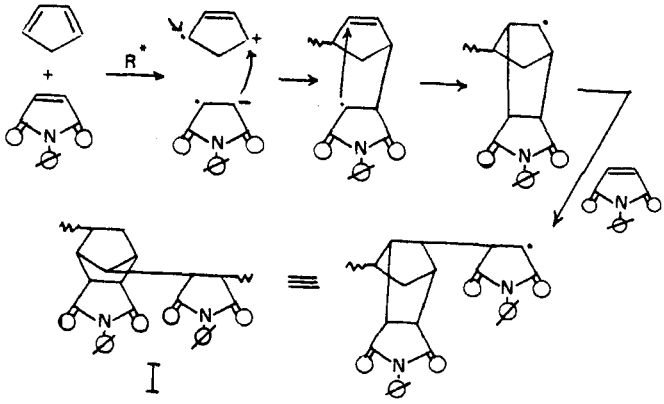
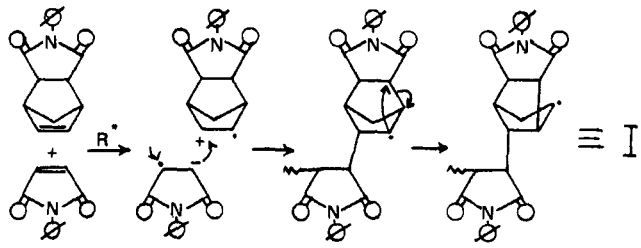
[2], the formation of the saturated 1:2 CPD-NPMI copolymers presumably proceeds through the cyclopolymerization of the excited 1:1 CPD-NPMI comonomer charge transfer complex, followed by the addition of NPMI, possibly excited NPMI*, as shown in Scheme 1.



SCHEME 1.

The copolymerization of the endo and exo CPD-NPMI Diels-Alder adducts with NPMI takes place under the same conditions that are effective in the copolymerization of CPD and NPMI and the homopolymerization of the CPD-NPMI adducts, i.e., in the presence of a radical catalyst undergoing rapid decomposition. Thus the excitation of the reactants presumably plays a role in the formation of the alternating copolymer. When the reaction is conducted below the endo-exo isomerization temperature, the copolymer retains the endo or exo configuration of the adduct. When the reaction is conducted above the isomerization temperature, the copolymer contains both endo and exo configurations. The proposed mechanism for the copolymerization of the CPD-NPMI adduct with NPMI is shown in Scheme 2.



SCHEME 2.

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The rapid rate of adduct formation from the interaction of CPD and NPMI at 150°C suggests that the copolymerization of CPD and NPMI to a 1:2 CPD-NPMI copolymer at such temperatures may proceed through the initial formation of the adduct, followed by its copolymerization with NPMI, as indicated above. The lower yields of copolymer obtained from the monomers at 80-90°C is also consistent with the expected lower rate of adduct formation at the lower temperature.

The higher molecular weight of the endo CPD-NPMI adduct-NPMI copolymer, i.e., 7508 representing a DP of 18, as compared with that of the 1:2 CPD-NPMI copolymer, i.e., 960-1374, representing a DP of 2-3, suggests that the adduct is not an intermediate in the copolymerization of CPD and NPMI. However, this is not conclusive since CPD is not present to act as a quencher in the adduct-NPMI copolymerization.

The homopolymerization of the endo and exo CPD-NPMI Diels-Alder adducts also requires the presence of a radical catalyst undergoing rapid decomposition. When the reaction is conducted below the endo-exo isomerization temperature, the polymer retains the endo or exo configuration of the adduct. When the reaction is conducted above the isomerization temperature, the polymer contains both endo and exo configurations.

The polymerization of the endo adduct takes place at 85°C in DCE on the addition of tBPP and at 120°C in CB on the addition of a 75% solution of tBPA in mineral spirits. Although the yields are relatively low, i.e., 9 and 16%, respectively, nevertheless, the formation of homopolymer from the endo adduct is in sharp contrast to the results obtained with the exo adduct, where no polymerization occurs under the same conditions. This reflects the greater ease of polymerization of the endo as compared with the exo adduct below 120°C. It is noteworthy that the exo adduct reportedly undergoes uncatalyzed, thermal polymerization to a greater extent than the endo adduct at temperatures above 250°C [16].

Both endo and exo adducts readily undergo homopolymerization at 120°C in CB when the tBPA catalyst is added as a 75% solution in benzene rather than as a solution in mineral spirits. This is in agreement with our earlier observations in the polymerization of MAH, wherein initiation by radical catalysts undergoing rapid decomposition resulted in higher conversions and/or higher molecular weight homopolymers when a photosensitizer such as benzene was present, although the reaction was conducted in the absence of light [5].

Assuming that exposure to excitation sources, e.g., species from the rapid decomposition of the catalyst, in the absence or in the presence of a photosensitizer, results in excitation of the double bond in the CPD-NPMI adduct and increases its susceptibility to radical attack, the homopolymerization of the adduct below the isomerization temperature may proceed as shown in Scheme 3 [14].

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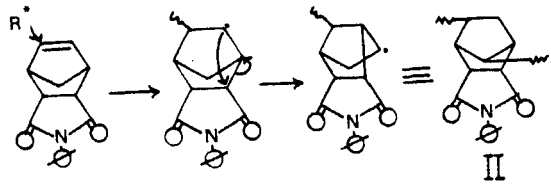

SCHEME 3.

The apparent participation of excited species in the homopolymerization of the endo and exo CPD-NPMI adducts leads to the suggestion that excited dimers are the polymerizable species, as earlier proposed in the homopolymerizations of ethylene [20-22] and MAH [23]. The proposed mechanism for the homopolymerization of the CPD-NPMI adducts below the endo-exo isomerization temperature is shown in Scheme 4.

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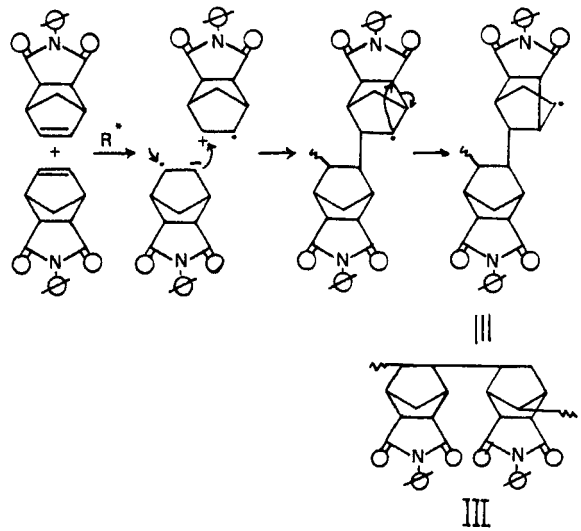
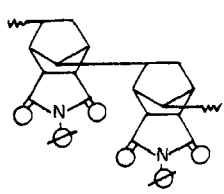
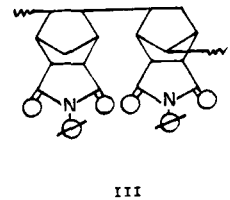


SCHEME 4.

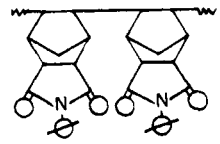
The polymer structure shown in Scheme 3 contains repeating units which are all rearranged (II). In contrast, the polymer structure shown in Scheme 4 contains repeating units which are alternatingly unrearranged and rearranged (III). Both structures differ from the all unrearranged structure (IV) proposed in the uncatalyzed, thermally induced polymerization of the CPD-NPMI adduct above the endo-exo isomerization temperature [16].



II



III



IV

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Due to retrograde dissociation of the adduct to CPD and NPMI at reaction temperatures of 250°C and higher, the product from the uncatalyzed, thermal reaction also contains units from NPMI and from the Diels-Alder reaction of the liberated CPD and the adduct [16].

Although the rearranged structure was earlier confirmed by 60 MHz ^{1}H-NMR analysis of the saturated product from the homopolymerization of norbornene [6], it has been applied without confirmation to the homopolymer of the CPD-MAH Diels-Alder adduct [8, 9] and suggested as an alternative structure for the product from the homopolymerization of the furan-MAH Diels-Alder adduct [4].

The broad, unresolved 60 MHz ^{1}H-NMR spectra of the homopolymers obtained from the CPD-MAH, F-MAH, and CPD-NPMI adducts do not permit confirmation or rejection of the proposed rearranged or partially rearranged structures. However, some insight may be obtained by consideration of the steric factors in the polymerization of the isomeric CPD-NPMI adducts.

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