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Anionic Polymerization of Dienyl Methacrylates[†]

Gerald D. Andrews

Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received May 3, 1983

ABSTRACT: Dienyl (2,4-hexadienyl, 1,3-cyclohexadienylmethyl, 4,7-octadienyl, etc.) methacrylate copolymers were prepared by anionic polymerization. The dienyl methacrylates were prepared by titanate-catalyzed transesterification of methyl methacrylate with dienols. These copolymers are useful new air-drying finish vehicles because they cross-link rapidly in air to give hard, durable films.

Anionic polymerization has been used to synthesize polymers with narrow molecular weight distributions, polymers with functional groups at the chain ends, block copolymers, and star polymers. These syntheses rely on the presence of a reactive carbanion at the end of each polymer molecule throughout the reaction, living polymerization. Another use of anionic polymerization, not yet fully exploited, is to synthesize polymers with radical-sensitive functional groups.

Linear poly(allyl methacrylate) has been prepared by anionic polymerization.[1] We became interested in copolymers of allyl methacrylate for use as air-drying finish vehicles because the high molecular weight homopolymer cross-links in air[1] or with free-radical initiators.[2] However, our initial work showed that the copolymers cross-link too slowly for many applications. The known chemistry of natural drying oils suggested that copolymers of dienyl methacrylates would cure faster.[3] Indeed, the copolymers can be prepared by anionic polymerization, and they cross-link rapidly on exposure to air to form hard, durable coatings.[4]

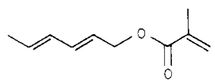
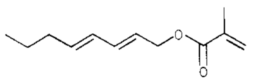
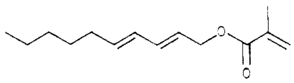
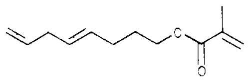
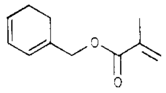
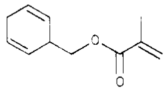
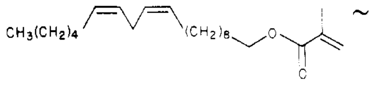
Results

Dienyl methacrylates can be synthesized by tetraisopropyl titanate catalyzed transesterification[5] of methyl methacrylate with dienols (Table I) in good yields. Diels–Alder reactions between the conjugated dienes and methacrylate vinyl groups do not occur significantly. Titanate catalysts are necessary because standard acidic and basic catalysts do not give good yields. For instance, strong bases convert 2,4-hexadienol to 2-hexenal, which leads to other byproducts.

The chemistry that we used to prepare highly structured methacrylate polymers[6] was used to prepare polymers from dienyl methacrylates. Addition of the monomer or monomer mixture to a solution of (1,1-diphenylhexyl)lithium in tetrahydrofuran at −78 °C produces the polymer in almost quantitative yield (100% conversion by NMR). The rate of polymerization if fast enough, relative to the addition time, that effectively random copolymers are produced. Side reactions are absent because the ester–enolate polymer end is not basic enough to polymerize conjugated dienes or isomerize 1,4-dienes. Free-radical polymerization of 2,4-hexadienyl methacrylate leads to insoluble, cross-linked products.

Polymers that we have prepared are described in Table II. The compositions were adjusted to give the copolymers glass transition temperatures near room temperature to improve film appearances. Proton NMR helped to characterize the polymers. The olefinic protons and the protons on methyl or methylene groups attached to oxygen are useful probes of composition. The 10 phenyl protons

Table I
Dienyl Methacrylates Prepared by Transesterification of the Corresponding Alcohol

methacrylate	structure	yield, %
2,4-hexadienyl		71
2,4-octadienyl		78
2,4-decadienyl		65
4,7-octadienyl		87
1,3-cyclohexadienyl- methyl		72
2,5-cyclohexadienyl- methyl		87
9,12-octadecadienyl		~100

[†] Contribution No. 3171.

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Table II
Dienyl Methacrylate Polymers and Copolymers Prepared As Described in the Text

methacrylates	mol % monomer feed	mol % monomer polymer	DP calcd	DP obsd	M_n/1000	M_w/M_n	T_g, °C
2,4-hexadienyl	100	100	10	12	1.5	1.8	
2,4-hexadienyl	15	15					
butyl	57	53	100	94	13	1.1	23
methyl	28	32					
2,4-octadienyl	15	15					
butyl	53	54	110	136	16	1.6	39
methyl	32	30					
2,4-decadienyl	15	16					
butyl	34	38	110	109	15	1.4	42
methyl	51	47					
4,7-octadienyl	15	17					
butyl	53	54	110	106	13	1.4	31
methyl	32	29					
1,3-cyclohexadienylmethyl	15	16					
butyl	53	55	110	121	13	1.5	47
methyl	32	29					
2,5-cyclohexadienylmethyl	15	13					
butyl	53	55	110	149	19	1.7	54
methyl	32	31					

on the diphenylhexyl group on each polymer molecule were used to estimate degree of polymerization (DP) by comparison with total monomer content. Gel permeation chromatography (GPC) estimates of M_n agree well with NMR-determined DP's.

These copolymers cross-link rapidly on exposure to air. Therefore, samples destined for NMR or GPC analysis were inhibited with phenothiazine. Polymers without inhibitors are best kept in solution to avoid cross-linking. Films of the neat of pigmented polymers exposed to air for less than 24 h become insoluble in what were initially good solvents. Typically, pigmented films that are air-dried for 24 h at room temperature have Knoop hardness values around 6 KHN, and films baked at 82 °C for 30 min have Knoop hardness above 15 KHN.[4]

The 2,5-cyclohexadienylmethyl methacrylate copolymer does not cross-link like the others. When it was heated with 0.1% cobalt accelerator at 70 °C for 24 h, neither the molecular weight nor the solubility of the polymer changed. The NMR spectrum of the recovered polymer shows that approximately half of the cyclohexadiene rings were oxidized to benzene rings. The difference in curing behavior between 2,5-cyclohexadienyl and the 1,3 isomer can be rationalized as follows. Radicals probably react with the 2,5-cyclohexadiene rings to abstract a hydrogen. Loss of another hydrogen leads to benzene. This is supported by the fact that 1,4-dihydrobenzoic acid reverts to benzoic acid on standing. Radicals probably add to the conjugated double-bond system of the 1,3-cyclohexadiene ring and lead to polymerization and thus cross-linking.

Experimental Section

2,4-Hexadienyl Methacrylate. A two-neck 500-mL flask equipped with a thermometer probe, stirring bar, and a 2.3 × 30 cm Vigreux column with variable-ratio take-off head was charged with 2,4-hexadienol (40.25 g, 0.41 mol, prepared by lithium aluminum hydride reduction of 2,4-hexadienal[7]), methyl methacrylate (175 mL, 1.65 mol), and phenothiazine (1 g). The mixture was boiled under nitrogen until no more water distilled. Tetraisopropyl titanate (2 mL) was added to the reflux ratio was adjusted to give a head temperature of 66 °C. About 50 mL of distillate, bp 66–96 °C, was collected over 1.5 h.

The unreacted methyl methacrylate was distilled at 39 °C (70 mm), and the product was distilled at 52–48 °C (1.2–0.5 mm) to give 48.72 g (71%) of colorless, liquid 2,4-hexadienyl methacrylate: IR (film) ν 3058, 2985, 1721, 1664, 1640, 1156 cm^{-1}; UV (isooctane) λ_{max} 227 nm (ϵ 30000); 220–MHz ^{1}H NMR revealed the presence of two isomers, major (86%) δ 6.22 (1 H, d of d, J = 10, 15 vinyl), 6.08 (1 H, br s, methacrylate vinyl), 6.0 (1 H, m, vinyl), 5.8–5.5 (2 H, m, vinyl), 5.51 (1 H, m, methacrylate vinyl), 4.62 (2 H, d, J = 6, OCH_2), 1.93 (3 H, br s, methacrylate methyl), 1.74 (3 H, d, J = 6, allylic methyl), minor (14%) δ 6.59 (d of d, J = 10, 14, vinyl), 4.68 (d, J = 6, OCH_2); 22.63-MHz ^{13}C NMR, major isomer δ 166.9, 136.6, 134.7, 130.8 (probably 2 carbons), 125.2, 124.2, 65.1, 18.3, 18.1. HPLC analysis (silica gel column, 1:1:0.001 methylene chloride–hexane–isopropyl alcohol, UV detector at 254 nm) showed less than 0.1% starting material in the product.

Anal.: C, 72.05; H, 8.61; P$^+$, 166.0975 (required for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; P$^+$, 166.0993).

Isomerically pure *trans,trans*-2,4-hexadienyl methacrylate was prepared on a 2.3-mol scale (69% yield) from *trans,trans*-2,4-hexadienol (Bedoukian Research, Inc.).

***trans,trans*-2,4-Octadienyl Methacrylate.** A reaction similar to the one above was run with *trans,trans*-2,4-octadien-1-ol (50.0 g, 0.40 mol, Bedoukian Research, Inc.), methyl methacrylate (170 mL, 1.6 mol), phenothiazine (1 g), and tetraisopropyl titanate (2 mL). After 2 h the methyl methacrylate was distilled, and the product was distilled at 73 °C (0.25 mm) to give 60.3 g (78%) of colorless, liquid *trans,trans*-2,4-octadienyl methacrylate: IR (film) ν 2985, 1712, 1631, 1449, 1310, 1287, 1149, 985, 962, 935, 811 cm^{-1}; UV (isooctane) λ_{max} 230 nm (ϵ 33000); 90-MHz ^{1}H NMR δ 6.4–5.4 (6 H, m, vinyl), 4.6 (2 H, d, J = 7, OCH_2), 2.05 (2 H, q, J = 7, allylic CH_2), 1.92 (3 H, m, allylic CH_3), 1.4 (2 H, sextet, J = 7, $CH_3\mathit{CH_2}CH_2$), 0.90 (3 H, t, J = 7, $\mathit{CH_3}CH_2$); 22.63-MHz ^{13}C NMR δ 166.9, 136.6, 136.2, 134.8, 129.6, 125.2, 124.3, 65.1, 34.8, 22.4, 18.3, 13.6.

Anal.: C, 74.09; H, 9.17; P$^+$, 194.1301 (required for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; P$^+$, 194.1305).

***trans,trans*-2,4-Decadienyl Methacrylate.** A reaction similar to the ones above was run with *trans,trans*-2,4-decadien-1-ol (50.0 g, 0.32 mol, Bedoukian Research, Inc.), methyl methacrylate (140 mL, 1.3 mol), phenothiazine (1 g), and tetraisopropyl titanate (2 mL). After 2 h the methyl methacrylate was distilled, and the product was distilled at 96–97 °C (0.2 mm) to give 46.4 g (65%) of colorless, liquid *trans,trans*-2,4-decadienyl methacrylate: IR (film) ν 2932, 1712, 1629, 1449, 1309, 1285, 1149, 984, 962, 933, 810 cm^{-1}; UV (isooctane) λ_{max} 230 nm (ϵ 29000); 90-MHz ^{1}H NMR δ 6.4–5.4 (6 H, m, vinyl), 4.63 (2 H, d, J = 7, OCH_2), 2.10 (2 H, q, J = 7, allylic CH_2), 1.97 (3 H, m, allylic CH_3), 1.3 (6 H, m, 3 CH_2), 0.90 (3 H, t, J = 6, $\mathit{CH_3}CH_2$); 22.63-MHz ^{13}C NMR δ 166.9, 136.5, 134.8, 129.4, 125.2, 124.3, 65.1, 32.7, 31.5, 29.0, 22.6, 18.3, 14.0.

Anal.: C, 75.82; H, 9.88; P$^+$, 222.1628 (required for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97; P$^+$, 222.1619).

Ethyl *trans*-4,7-Octadienoate.[8] A 500-mL flask equipped with a 30-cm Vigreux column was charged with 1,5-hexadien-3-ol (Aldrich, 24.82 g, 0.25 mol), triethyl orthoacetate (221 g, 1.36 mol, Aldrich), and propionic acid (1.11 g, 15 mmol). Ethanol (35 mL, 0.6 mol) was distilled from the mixture at bp 78–79 °C over 1 h while the pot temperature rose from 108 to 146 °C. The excess triethyl orthoacetate was distilled at 54 °C (25 mm), and the residue was distilled at 101–104 °C (25 mm) to give 37.1 g (87%) of colorless, liquid ethyl *trans*-4,7-octadienoate. Another run with twice as much 1,5-hexadien-3-ol gave an 80% yield: 90-MHz ^{1}H NMR δ 5.8 (1 H, m, $\mathit{H}C{=}CH_2$), 5.43 (2 H, m, HC=CH), 5.15–4.85 (2 H, m, $H_2C{=}C$), 4.07 (2 H, g, J = 7, OCH_2e, 2.70 (2 H, m, doubly allylic CH_2), 1.33 (4 H, s, CH_2CH_2), 1.23 (3 H, t, J = 7, CH_3); 22.63-MHz ^{13}C NMR δ 172.7, 137.1, 129.7, 129.1, 115.1, 60.1, 36.7, 34.3, 28.1, 14.4.

Anal.: C, 71.23 and 70.92; H, 9.58 and 9.56; P$^+$, 168.1153 (required for $C_{10}H_{12}O_2$: C, 71.39; H, 9.59; P$^+$, 168.1149).

***trans*-4,7-Octadienol.** Lithium aluminum hydride (3.7 g, 98 mmol) reduction of the above ester (30.0 g, 0.18 mol) in ether (250 mL) followed by standard workup gave 20.8 g (92%) of *trans*-4,7-octadienol, bp 100–102 °C: 90-MHz ^{1}H NMR δ 5.8 (1 H, m, $\mathit{H}C{=}CH_2$), 5.43 (H, m, HC=CH), 5.03 (1 H, d of m, *trans*-

$H_2C{=}C$), 4.90 (1 H, m, *cis*-$H_2C{=}C$), 3.60 (2 H, t, $J = 6$, OCH_2), 2.77 (2 H, m, doubly allylic CH_2), 2.5 (1 H, s, OH), 2.10 (2 H, m, allylic CH_2), 1.63 (2 H, quintet, $J = 7$, $OCH_2CH_2CH_2$); 22.63-MHz ^{13}C NMR δ 137.3, 131.0, 128.2, 114.9, 61.9, 36.8, 32.4, 28.9.

Anal.: 10.88; P^+, 126.1051 by GC/MS (required for $C_8H_{14}O$: C, 76.14; H, 11.18; P^+, 126.1044).

***trans*-4,7-Octadienyl Methacrylate.** A reaction similar to the ones above was run with *trans*-4,7-octadien-1-ol (18.53 g, 0.146 mol), methyl methacrylate (58.8 g, 0.59 mol), phenothiazine (0.5 g), and tetraisopropyl titanate (1.0 mL). When the head temperature had risen to 96 °C (pot temperature of 117 °C), the methyl methacrylate was distilled, and the product was distilled at 64–65 °C (0.2 mm) to give 24.8 g (87%) of colorless, liquid *trans*-4,7-octadienyl methacrylate: IR (film) ν 2950, 1712, 1629, 1445, 1311, 1287, 1156, 964, 933, 907, 810 cm^{-1}; UV (isooctane) end absortion; 220-MHz ^1H NMR δ 6.06 (1 H, br s, methacrylate vinyl), 5.76 (1 H, m, $HC{=}CH_2$), 5.50 (1 H, m, methacrylate vinyl), 5.41 (2 H, m, $HC{=}CH$), 5.02–4.92 (2 H, m, $HC{=}CH_2$), 4.11 (2 H, t, $J = 6$, OCH_2), 2.72 (2 H, m, doubly allylic CH_2), 2.10 (2 H, m, allylic CH_2), 1.95 (3 H, m, allylic CH_3), 1.73 (2 H, quintet, $J = 6$, $OCH_2CH_2CH_2$); 22.63-MHz ^{13}C NMR δ 167.2, 137.1, 136.7, 130.2, 128.9, 124.9, 115.0, 64.1, 36.8, 29.1, 28.6, 18.3.

Anal.: C, 74.49; H, 9.11; P^+, 194 (required for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; P^+, 194).

1,3-Cyclohexadienylmethyl Methacrylate. A reaction similar to the ones above was run with 1,3-cyclohexadienylmethanol[9] (20.49 g, 0.182 mol), methyl methacrylate (73.0 g, 0.73 mol), phenothiazine (0.1 g), and tetraisopropyl titanate (1.0 mL). After 1.5 h, the head temperature had risen to 98 °C. The methyl methacrylate was distilled, and the product was distilled at 56–43 °C (0.1–0.55 mm) to give 23.99 g (72%) of colorless, liquid 1,3-cyclohexadienylmethyl methacrylate: IR (film) ν 3067, 2950, 1715, 1633, 1449, 1311, 1287, 1149, 1058, 1006, 9358, 862, 810, 746 cm^{-1}; UV (isooctane) λ_{max} 261 nm (ϵ 7090); 90-MHz ^1H NMR δ 6.10 (1 H, m, methacrylate vinyl), 5.9–5.6 (3 H, m, vinyl), 5.5 (1 H, m, methacrylate vinyl), 4.60 (2 H, s, OCH_2), 2.2 (4 H, m, CH_2CH_2), 1.97 (3 H, m, allylic CH_3); 22.63-MHz ^{13}C NMR δ 166.8, 136.6, 133.1, 126.2, 125.2, 124.0, 121.9, 67.5, 23.7, 22.7, 18.3.

Anal.: C, 74.10; H, 8.04; P^+, 178.1001; $(P - 2)^+$, 176.0846 (178:176 ratio, 4:1) (required for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; P^+, 178.0994; $(P - 2)^+$, 176.0836).

2,5-Cyclohexadienylmethyl Methacrylate. A reaction similar to the ones above was run with 2,5-cyclohexadienylmethanol[10] (40.86 g, 0.37 mol, 13% 2-cyclohexenylmethanol), methyl methacrylate (159 mL, 1.5 mol), phenothiazine (0.1 g), and tetraisopropyl titanate (2 mL). After the reaction was done, the methyl methacrylate was distilled, and the product was distilled at 58–54 °C (0.15–0.12 mm) to give 57.5 g (87%) of colorless, liquid 2,5-cyclohexadienylmethyl methacrylate: IR (film) ν 3030, 2941, 1709, 1629, 1445, 1309, 1287, 1152, 1009, 979, 934, 873, 810 cm^{-1}; 220-MHz ^1H NMR δ 6.07 (1 H, m, methacrylate vinyl), 5.8 (2 H, m, vinyl), 5.6 (2 H, m, vinyl), 5.50 (1 H, m, methacrylate vinyl), 4.04 (2 H, d, $J = 6$, OCH_2), 3.1 (1 H, m, allylic methine), 2.6 (2 H, m, allylic methylene), 1.93 (3 H, m, allylic CH_3) (the 13% impurity of cyclohexenylmethyl methacrylate gave broad signals from δ 2.0 to 1.3 and a 6-Hz doublet (CH_2O) at 4.02); 22.63-MHz ^{13}C NMR δ 167.1, 137.7, 126.3, 125.4, 125.2, 68.0, 35.7, 26.5, 18.3.

Anal.: C, 74.23; H, 8.11; P^+, 178.0977; $(P - 2)^+$, 176.0843 (required for 13% $C_{11}H_{16}O_2$ + 87% $C_{11}H_{14}O_2$: C, 74.02; H, 8.05; $C_{11}H_{14}O_2$ requires *m/e* 178.0993 and $C_{11}H_{12}O_2$ requires *m/e* 176.0837).

***cis,cis*-9,12-Octadecadienyl Methacrylate.** A reaction similar to the ones above was run with *cis,cis*-9,12-octadecadien-1-ol (25.0 g, 9.38 mmol, Sigma), methyl methacrylate (40 mL, 38 mmol), phenothiazine (0.1 g), and tetraisopropyl titanate (1 mL). When the head temperature had risen to 99 °C (pot temperature of 112 °C), the reaction mixture was cooled and then filtered through alumina (30 g, Woelm activity grade I) with ethyl acetate rinses. The filtrate was concentrated on a rotary evaporator and then at 0.5 mm to give 32.4 g (100%) of light yellow *cis,cis*-9,12-octadecadienyl methacrylate: 90-MHz ^1H NMR δ 6.03 (1 H, br s, methacrylate vinyl), 5.47 (1 H, m, methacrylate vinyl), 5.30 (4 H, m, vinyl), 4.09 (2 H, t, $J = 7$, OCH_2), 2.75 (2 H, broad t, $J \sim 6$, doubly allylic CH_2), 2.2–1.1 (27 H, me, 0.8. (3 H, *t*, $J \sim 6$, $-CH_2CH_3$). HPLC analysis (90:10:1 CH_2Cl_2–ethyl acetate–isopropyl alcohol, silica gel column, refractive index detector) showed that all of the starting material was gone.

Anal.: P^+, 334.2864 ($C_{22}H_{38}O_2$ requires 334.2864).

2,4-Hexadienyl Methacrylate (15 mol %)/*n*-Butyl Methacrylate (57 mol %)/Methyl Methacrylate (28 mol %) Random Copolymer. This is the general procedure used for the preparation of the polymers listed in Table II. All glassware was oven dried at 150 °C for at least 4 h, assembled while hot, flushed with dry argon until cool, and maintained under a positive pressure of argon. The tetrahydrofuran was freshly distilled from benzophenone/sodium. Freshly distilled 2,4-hexadienyl methacrylate (bp 38 °C (0.07 mm), 17.46 g, 0.105 mol), *n*-butyl methacrylate (bp 66 °C (20 mm), 56.88 g, 0.400 mol), and methyl methacrylate (bp 101 °C, 19.55 g, 0.195 mol) were mixed, filtered through alumina (10 g, as above), and deoxygenated with a slow stream of argon for 15 min.

A 500-mL, four-neck flask equipped with a glass mechanical stirrer, thermometer probe, and rubber septum was charged with tetrahydrofuran (300 mL) and 1,1-diphenylethylene (0.8 mL, 4.5 mmol, redistilled, Aldrich) via syringe. The solution was cooled to 5 °C and butyllithium (1.5 m in hexane, 3.0 mL, 4.5 mmol, Foote) was added via syringe. The blood red solution was cooled to −78 °C in a dry ice–acetone bath. The monomer mixture (74 mL, 0.5 mol, 67.1 g) was added at a rate that kept the temperature of the solution below −70 °C (15 min). After the first few drops of monomer was added, the solution faded to light yellow and remained that way during the rest of the addition. After monomer addition, the solution was stirred 15 min, acetic acid (0.5 mL, 8 mmol) was added, and the colroless solution was warmed to room temperature. A 10-g aliquot was removed for analysis. The remainder was suction filtered through diatomaceous filter-aid (Celite) in a medium-porosity Büchner funnel and concentrated to 100.4 g (68% solids) on a rotary evaporator. The residue was diluted with butyl Cellosolve (70 g) to make a 40% solids solution for preparation of test films.

Phenothiazine (10 mg) was added to the aliquot and it was poured into 500 mL of rapidly stirred water. The solid product was filtered and then dried at 0.5 mm overnight: 90 HMHz ^1H NMR (10% w/w in $CDCl_3$) δ 7.1 (br s, phenyl, integral 1.8), 6.4–5.4 (m, vinyl, integral 11), 4.43 (br d, $J = 6$, OCH_2CH, integral 5), 3.93 (br t, $J \sim 6$, OCH_2CH_2, integral 18), 3.77 (br s, OCH_3, integral 16), 2.2–1.4 (m, integral 163). These integrals correspond to 15% 2,4-hexadienyl, 53% butyl, and 32% methyl methacrylate in a copolymer of DP 94; GPC $M_n = 13\,000$; $M_w = 14\,000$; $M_w/M_n = 1.09$; T_g (by DSC, four heats, 10 °C/min, under N_2) 23 °C.

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