

Synthesis of Tung Oil–Diacrylate Copolymers via the Diels–Alder Reaction and Properties of Films from the Copolymers

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ABSTRACT: Copolymers were synthesized from tung oil and 1,6 hexanediol diacrylate or 1,4-butanediol diacrylate via the Diels–Alder reaction. The copolymers were completely soluble in common laboratory solvents, and had very broad molecular weight distributions. The residual double bonds in the copolymers were used to cure films by oxidative means. The films had good solvent resistance, good gloss, and a reasonable hardness–flexibility balance. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2369–2375, 2001

Key words: tung oil; Diels–Alder reaction; copolymers

INTRODUCTION

Drying and semidrying oils have been used extensively in the paint and coatings industry for the last several decades.^{1–4} Such oils are primarily used in the synthesis and formulation of oxidatively curable coatings. Tung oil, because of its high level of unsaturation is classified as a drying oil.⁵

For many applications the large number of double bonds in tung oil makes the oil too reactive. When used alone or in high concentrations in blends, tung oil often cures so rapidly that a highly wrinkled surface results. Because this wrinkling ruins the appearance of a coating, it is often necessary to modify the reactivity of tung oil. The reactivity can be modified by chemical means such as copolymerization with styrene; this reduces the number of double bonds/oil moiety and makes the cure speed of the resulting

copolymer more reasonable.^{6,7} However, care must be taken to avoid gelation in these copolymerizations.

Tung oil is also known to undergo the Diels–Alder reaction with facility.^{8,9} We thought then that a tung oil–diacrylate reaction could be used to generate copolymers in which the double bond content of the tung oil moiety had been reduced. Also, because such a polymerization is not a chain addition polymerization, gelation can easily be avoided by controlling comonomer stoichiometry and sufficient residual double bonds should remain so that oxidative cure of films of the copolymer(s) would be possible.

EXPERIMENTAL

General

All reagents and solvents used in this study were obtained from Aldrich, and were used as received. Nuclear magnetic resonance spectra were obtained at ambient temperature on CDCl₃ solutions of ma-

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Table I Copolymerization Conditions and Copolymer Data

Polymer ^a	Mol of Tung Oil in Feed	Mol of 1,6-HDDA in Feed ^b	Mol of 1,4-BDDA in Feed ^b	Solvent	% Conversion	<i>T_g</i> (°C)
TOHD1	0.06	0.03	—	—	77.5	—
TOHD2	0.18	0.16	—	—	76.3	-53
TOHD3	0.18	0.18	—	—	58.6	-49
TODH4	0.13	0.075	—	BOE ^c	50.0	—
TOBD1	0.24	—	0.14	—	63.8	-60

^a TOHD = tung oil-hexanediol diacrylate; TOBD = tung oil-butanediol diacrylate.

^b 1,6-HDDA = 1,6-hexanediol diacrylate; 1,4 BDDA = 1,4-butanediol diacrylate.

^c BOE = 2-butoxyethanol.

terial using a Varian Gemini 300 FT NMR. Infrared spectra were recorded on films of material cast on NaCl plates or on KBr pellets using a Nicolet 5DXB FTIR. Molecular weights were measured using a GPC equipped with a Waters 510 pump, 410 RI detector and two Polymer Labs 30-cm linear columns. Tetrahydrofuran was used as the eluent, and numerical values for the molecular weights were generated by comparison to a polystyrene calibration curve. Glass transition temperature measurements were made with a TA Instruments 2990 DSC. Film cure was assessed by measuring resistance to methyl ethyl ketone using a double-rub technique. The test was performed with an Atlas AATCC Crockmeter. Gloss was measured with a BYK-Gardner Microtrigloss meter. Impact resistance was measured with a Gardner Impact Tester

employing a 4-lb. weight. Pencil hardness measurements were made according to ASTM D3363.

Copolymer Synthesis

Bulk copolymers were synthesized by weighing the desired amounts of tung oil (Fig. 1) and diacrylate into a 250-mL flask equipped with a mechanical stirrer, reflux condenser, nitrogen inlet, and thermometer. Hydroquinone (1.3 wt %) was added to inhibit free radical addition polymerization, and heating to 150° under a slow flow of nitrogen was started. At 125–130° an exotherm occurred that caused the temperature of the reaction mixture to rapidly increase to 165° before external heating could be discontinued. The duration of the exotherm was typically 15–20 min. When the temperature of

Table II Time-Conversion Results

Polymer	Mol of Tung Oil in Feed	Mol of 1,6 HDDA in Feed	Mol of 1,4 BDDA in Feed	Pzn Temp. (°C)	Pzn Time (Min)	% Conversion
TOHD5	2.8×10^{-2}	1.4×10^{-2}	—	150	30	72.0
TOHD6	2.8×10^{-2}	1.4×10^{-2}	—	150	60	77.5
TOHD7	2.8×10^{-2}	1.4×10^{-2}	—	150	90	79.0
TOHD8	2.8×10^{-2}	1.4×10^{-2}	—	150	120	82.8
TOHD9	2.8×10^{-2}	1.4×10^{-2}	—	150	150	80.8
TOHD10	2.8×10^{-2}	1.4×10^{-2}	—	130	30	65.3
TOHD11	2.8×10^{-2}	1.4×10^{-2}	—	130	60	62.0
TOHD12	2.8×10^{-2}	1.4×10^{-2}	—	130	90	64.4
TOHD13	2.8×10^{-2}	1.4×10^{-2}	—	130	120	64.0
TOHD14	2.8×10^{-2}	1.4×10^{-2}	—	130	150	65.0
TOBD2	3.4×10^{-2}	—	1.7×10^{-2}	150	30	60.0
TOBD3	3.4×10^{-2}	—	1.7×10^{-2}	150	60	73.2
TOBD4	3.4×10^{-2}	—	1.7×10^{-2}	150	90	71.0
TOBD5	3.4×10^{-2}	—	1.7×10^{-2}	150	120	74.3
TOBD6	3.4×10^{-2}	—	1.7×10^{-2}	150	150	79.5

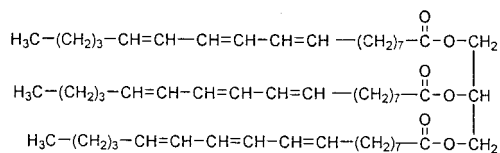


Figure 1 Tung oil structure.

the reaction mixture had fallen to 140°, external heating was resumed. The reaction mixture was heated at 150° for 5.5 h. On cooling to ambient temperature the entire contents of the flask solidified. The solid mass was dissolved in 200 mL of CHCl_3 , and the polymer was precipitated by adding this solution to an eightfold excess of CH_3OH . The polymer was purified by two reprecipitations from CHCl_3 into CH_3OH . The polymers were dried *in vacuo* at 35° for 96 h, then weighed to determine conversions.

Solution copolymers were synthesized in the same manner as the bulk copolymers except that sufficient 2-butoxyethanol was added to the reaction flask to give a 60 wt % monomer solution. Copolymer purification was the same as the bulk copolymer purification.

Time-conversion copolymerizations were conducted in bulk using air-tight vials. The vials were removed from a constant temperature bath at various time intervals, the contents were cooled to ambient temperature, diluted with CHCl_3 and added to CH_3OH to precipitate the polymer. The copoly-

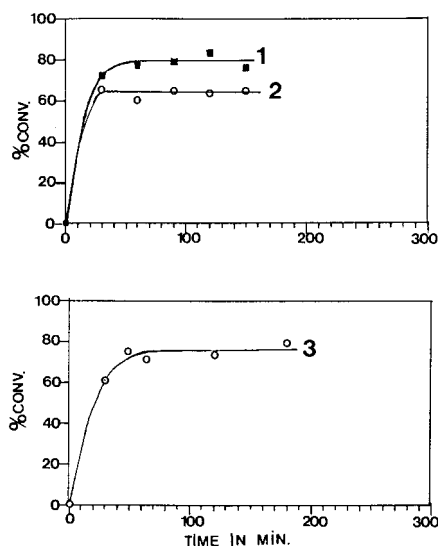


Figure 2 Time-conversion curves: (1) TOHD 5-9; (2) TOHD 10-14; (3) TOBD 2-6.

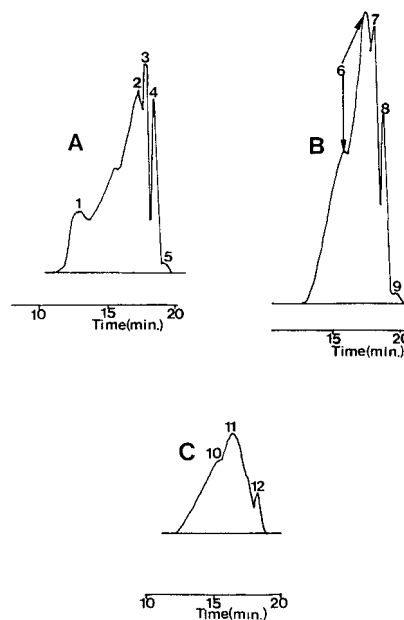


Figure 3 GPC chromatograms: (A) TOHD 1; (B) TOHD 2; (C) TOHD 3.

mers were purified by reprecipitation from CHCl_3 into CH_3OH , dried to a constant weight, and conversions were determined gravimetrically.

Coatings

Copolymer (25 g) was dissolved in 75 g of methyl ethyl ketone. This solution was divided into two equal parts by weight and cobalt naphthenate (2.5×10^{-2} g) and manganese naphthenate (2.5×10^{-3} g) were added to one part. The solution with no added catalyst would serve as a control. Both catalyzed and uncatalyzed solutions were drawn over aluminum or Bonderite 1000 panels with a

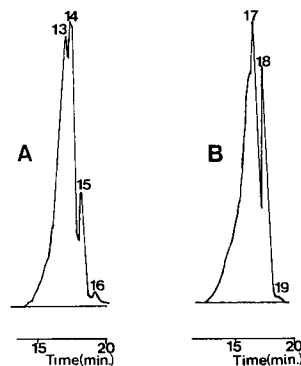


Figure 4 GPC chromatograms: (A) TOHD 4; (B) TOBD 1.

Table III Copolymer Molecular Weights and Molecular Weight Distributions

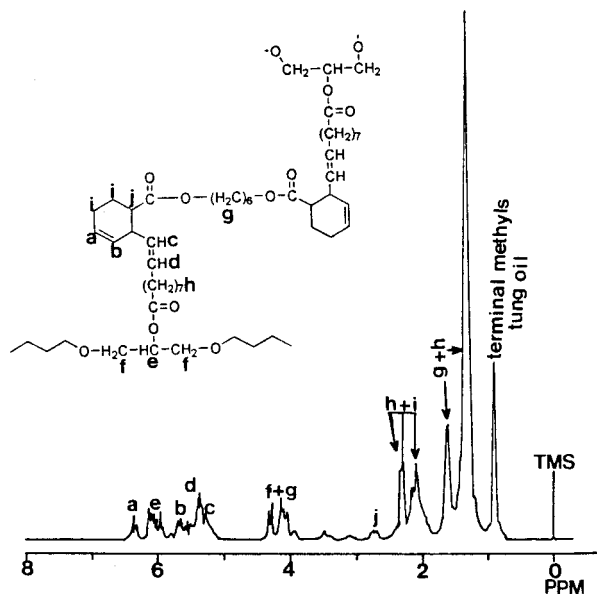
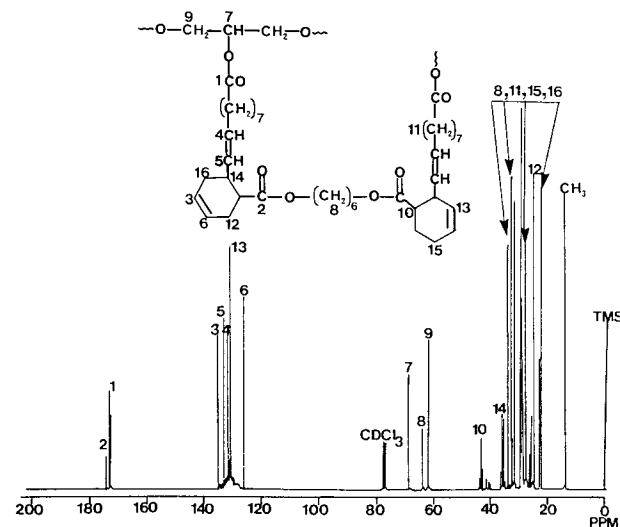
Polymer	Peak Number	M_n	M_w	M_w/M_n	Percent of Total Peak Area
TOHD1	1	1.2×10^6	1.6×10^6	1.33	13.0
TOHD1	2	1.4×10^4	7.1×10^4	5.07	64.0
TOHD1	3	2.9×10^3	3.1×10^3	1.07	13.0
TOHD1	4	1.3×10^3	1.4×10^3	1.08	9.4
TOHD1	5	570	580	1.02	0.5
TOHD2	6	1.3×10^4	8.0×10^4	6.15	76.7
TOHD2	7	2.9×10^3	3.2×10^3	1.10	13.6
TOHD2	8	1.4×10^3	1.5×10^3	1.07	9.0
TOHD2	9	500	520	1.04	0.7
TOHD3	10	1.3×10^4	1.4×10^5	10.77	93.5
TOHD3	11	1.5×10^3	1.6×10^3	1.07	5.5
TOHD3	12	590	620	1.05	1.0
TOHD4	13	8.4×10^3	1.8×10^4	2.14	65.0
TOHD4	14	2.9×10^3	3.1×10^3	1.07	24.2
TOHD4	15	1.4×10^3	1.6×10^3	1.14	9.2
TOHD4	16	480	570	1.08	1.6
TOBD1	17	5.2×10^3	1.6×10^4	3.08	81.0
TOBD1	18	1.3×10^3	1.4×10^3	1.08	18.4
TOBD1	19	430	460	1.07	0.6

#3 Bird bar to give films. Dry film thicknesses were 1.3–1.5 mil. Some of the panels were baked in an oven at 130°C for varying lengths of time, and some of the panels were stored at an ambient temperature, with film properties being evaluated periodically. The panels from the oven were allowed to cool to ambient temperature, and the films were tested immediately for property devel-

opment. One of the baked films was also tested for properties after storage at ambient temperature for a given amount of time.

Solvent Extraction

For these experiments a 250–300 mg sample of a film was added to a clean, dry screw cap vial. Tetrahydrofuran (10 g) was then added, and the vial was tightly sealed with a Teflon-lined screw cap.

**Figure 5** 300 MHz ^1H -NMR spectrum of TOHD3.**Figure 6** 75.5 MHz ^{13}C -NMR spectrum of TOHD3.

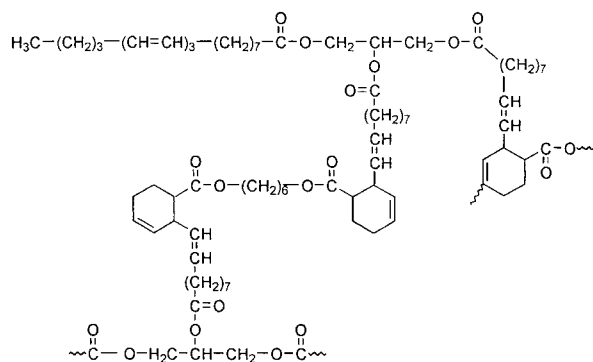


Figure 7 Idealized copolymer structure.

This mixture was allowed to stand, with periodic agitation, at ambient temperature for 7 days. Any remaining solid was isolated by filtration and dried *in vacuo* at 35°C to a constant weight.

RESULTS AND DISCUSSION

Table I lists the polymerization conditions and some polymer characterization data.

Table II lists the results of the time-conversion experiments. The results presented in Table II are shown plotted in Figure 2.

Relatively high yields of methanol-insoluble products are obtained early in the reaction; there is very little if any change in copolymer yield after

60 min of reaction time. As expected, reaction temperature is a factor. Higher maximum conversions are obtained at 150° than at 130°. Within experimental error, the maximum conversions for the 1,6-HDDA and 1,4-BDDA comonomers are equal.

All the copolymerizations produced material with broad, multimodal molecular weight distributions. The multimodality persisted even after two reprecipitations. The GPC chromatograms of the polymers listed in Table I are shown in Figures 3 and 4. The molecular weights and molecular distributions corresponding to each numbered peak are listed in Table III.

The molecular weights and molecular weight distributions obtained for the copolymers produced in the time-conversion experiments were very similar to those listed in Table III.

In some cases, very high molecular weight fractions are produced, and the overall molecular weight distributions are very broad in all cases. The viscosity of the medium is somewhat responsible for the molecular weight distributions obtained. As high conversions are reached fairly rapidly, the relative viscosity of the medium increases rapidly. In turn, this causes variations in local concentrations of reactive species that will broaden molecular weight distributions. The viscosity increase could also be why the limit of conversion seems to be ~ 80%, even at long reac-

Table IV Film Properties

Coating	Copolymer	Substrate	Catalyst ^a	Bake Temp. (°C)	Bake Time (Min)	Methyl Ethyl Ketone Double Rubs	Pencil Hard.	F.I. ^b in lbs.	R.I.	60° Gloss
1	TOHD1	A1	Y	130	30	15	F	—	—	80
2	TOHD1	A1	Y	130	90	25	F	—	—	80
3	TOHD1	A1	Y	130	180	37	H	—	—	77
4	TOHD3	B1000	Y	130	30	40	2H	40	20	80
5	TOHD3	B1000	Y	130	90	50	4H	40	20	88
6	TOHD3	B1000	Y	130	180	65	4H	20	10	87
7	TOHD3	B1000	N	130	180	5	—	—	—	—
8	TOHD3	B1000	Y	22 ^c	—	20	F	80	60	86
9	TOHD3	B1000	Y	130 ^d	30	150	5H	20	5	88
10	TOHD2	B1000	Y	22 ^e	—	40	F	60	40	85

^a Y = Yes, N = No.

^b F.I. = Forward impact; R.I. = reverse impact. Impact testing is not done on aluminum as the metal itself is not hard enough and can give way before the film does.

^c Sample left at ambient temperatures for 7 days, then evaluated for properties.

^d Sample 4 reevaluated after 30 days at ambient temperature.

^e Sample left at ambient temperature for 30 days.

tion times. In contrast, the reaction conducted in solution, TOHD4, yielded a principle fraction with a relatively narrow molecular weight distribution. This is expected, as the solvent should provide a more uniform concentration of reactants, resulting in no very high molecular weight species and narrower molecular weight distributions.

Figures 5 and 6 show representative ^1H - and ^{13}C -nmr spectra of a tung oil-1,6-HDDA copolymer (TOHD3). Assignments of the resonances are given in the figures. The assignments were made by comparisons to literature spectra and by computer simulation.^{8,10} While not all resonances could be assigned, the spectra support a structure for the polymer like that shown in Figure 7.

The properties obtained from the films are listed in Table IV. Table V lists the results of the solvent extraction studies.

The film properties and the solvent extraction studies show that the films are curing, although somewhat slowly, at ambient temperature. Better films are obtained if the films are baked first, then left at ambient temperature for some period of time. This is typical of oxidative cures, and the infrared spectra shown in Figure 8 indicates¹¹ that cure is oxidative. The cured film shows a large absorbance at 3480 cm^{-1} . This absorbance is most likely due to $-\text{OH}$ groups. If the tung oil-diacrylate copolymers are curing oxidatively, through the remaining double bonds, the accepted mechanism for such a cure shows that a large number of $-\text{OH}$ groups should be produced.¹² Because this seems to be the case, it is reasonable to conclude that the films are indeed curing oxidatively.

CONCLUSIONS

We have shown that it is possible to produce high molecular weight polymers through a Diels-Alder

Table V Solvent Extraction Studies

Polymer Film	% Insoluble Material
3	42.3
4	44.0
6	69.6
7	0.0
9	94.5

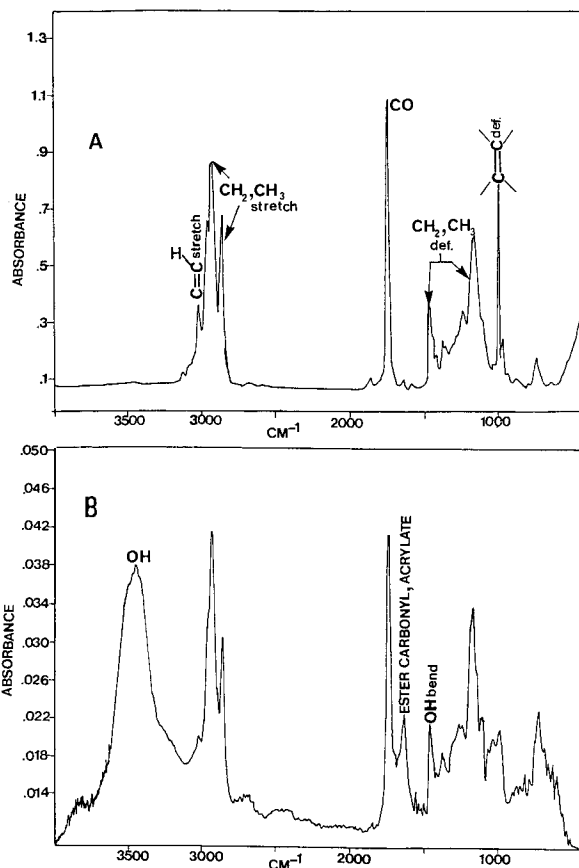


Figure 8 FTIR spectra: (A) Tung oil; (B) Cured Tung Oil-1,6 HDDA film (film 9).

reaction of tung oil with diacrylate monomers. The polymers produced are completely soluble, so no acrylate-acrylate chain addition polymerization has taken place. The molecular weight distributions of the copolymers are broad and multimodal, even after purification. In some cases, very high molecular weight fractions are produced, but, numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve so they may not be considered as absolutely accurate. Films of the copolymers were readily prepared, and when cured, had good solvent resistances, high hardnesses, and good glosses. The cure reaction seems to continue at ambient temperature for a period of at least 30 days. Infrared spectroscopy shows that the films cure oxidatively as intended.

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REFERENCES

1. Nylen, P.; Sunderland, E. *Modern Surface Coatings*; Wiley Interscience: New York, 1965.
2. Larson, E. C.; Sipple, H. E. *J Paint Technol* 1967, 39, 259.
3. Thames, S. F.; Long, J. S.; Smith, O. D.; Jen, S.; Evans, J. M. *J Am Oil Chem Soc* 1967, 45, 277.
4. Hoffman, J. S.; Bickford, W. G. *New Tung Oil Der.*, USDA, Southern Regional Research Laboratory, 1956.
5. DeWit, J. *Org Coat Si Technol*, 7, Parfitt, G. D., Patisis, A. V., Ed. Marcel Dekker: New York, 1984.
6. Brunner, H.; Tucker, D. R. *Research* 1949, 2, 42.
7. Brunner, H.; Tucker, D. R. *J Appl Chem* 1951, 1, 563.
8. Evans, J. L. Ph.D. Dissertation, Univ. of Southern Miss., 1970.
9. Wasserman, A. *Diels-Alder Reactions*; Elsevier: London, 1965.
10. In-house computer simulation program, S.C. Johnson Polymer, 1994.
11. Silverstein, R. M.; Bassler, G. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1967.
12. Oldring, P. K. T.; Hayward, G., Eds. *Resins for Surface Coatings*; SITA Technol. London, 1987, vol. 1.