

Copolymerization Behavior of 3-Isopropenyl- α,α -Dimethylbenzylamine and a Preliminary Evaluation of the Copolymers in Thermoset Coatings

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ABSTRACT: The title monomer was synthesized from 3-isopropenyl- α,α -dimethylbenzyl isocyanate in a significantly better yield than was previously reported. 3-Isopropenyl- α,α -dimethylbenzylamine proved incapable of homopolymerization using free-radical initiation but readily copolymerized with a variety of commonly available monomers under free-radical conditions. Films of some of the copolymers were prepared and crosslinked using a variety of multifunctional epoxy compounds. The films had good solvent resistance, high hardness, and good gloss. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1030–1039, 2001

Key words: reactivity ratios; thermoset coatings; amine monomer

INTRODUCTION

The importance of synthesizing polymers containing moieties capable of participating in postpolymerization reactions continues to increase in today's coating industry. A primary reason for this is that producing coating systems with lower volatile organic compound (VOC) content is imperative.^{1–4} To lower the VOC content but maintain good film-formation properties, polymers with lower glass transition temperatures are usually employed. This leads to softer films which can have inferior properties, for example, less block resistance, increased pickup of atmospheric contaminants, and less mar resistance. One approach to combating these problems is the use of polymers containing moieties which can participate in crosslinking reactions after the film is formed. Crosslinking increases the film's T_g , resulting in better block resistance and less dirt pickup.

We have been investigating the synthesis and coatings properties of functional copolymers for quite some time,^{5–9} and we now report the results that we have obtained with an amine functional copolymer. 3-Isopropenyl- α,α -dimethylbenzylamine (IDBA) was first synthesized by Kania et al. in 1989.¹⁰ The starting material was 3-isopropenyl- α,α -dimethylbenzyl isocyanate (m-TMI, Cytec, Stamford, CT). The synthetic procedure employed was somewhat unwieldy and the yields of IDBA obtained were low. Additionally, a detailed study of the copolymerization behavior of IDBA was not reported. Because amines are very reactive moieties capable of undergoing reactions with a wide variety of species over a broad range of conditions, we undertook a study aimed at synthesizing IDBA in higher yield and evaluating the copolymerization behavior of the monomer. We also evaluated the performance of IDBA copolymers in films as a way to validate the other parts of our study.

EXPERIMENTAL

All solvents and other chemicals used in this work were obtained from commercial sources and were

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Table I Lauryl Methacrylate Copolymers

Polymer	Styrene (mol %)	LMA ^a (mol %)	IDBA (mol %)	Polymerization Time (h)	Polymerization Temperature (°C)	Percent Conversion	M_n	M_w
1	64.0	18.0	18.0	4.0	18.0	100	6400	10,300
2	74.5	17.0	8.5	4.0	18.0	100	3400	23,000
3	78.9	17.0	4.1	4.0	18.0	100	6450	29,000

^a LMA, lauryl methacrylate.

used as received. Molecular weights were measured using a GPC equipped with a Waters 510 pump, 410 RI detector, and two 30-cm Polymer Labs linear columns. The GPC was calibrated with narrow molecular weight polystyrene standards. Copolymer compositions were determined by ¹H-NMR spectroscopy. Spectra were obtained on CDCl₃ solutions of material at ambient temperature with a Varian Gemini 300 FT NMR. Solvent resistance, as an estimation of the degree of cure, was measured by counting the number of methyl ethyl ketone double rubs required to break through a film to the substrate below. The test was performed with an ATLAS AATCC crockmeter.

Forward impact resistance was measured with a Gardner impact tester employing a 4-lb weight. Gloss was measured with a BYK-Gardner microtrigloss meter. Pencil hardness measurements were made according to ASTM D3363. Infrared spectroscopy was performed with a Nicolet 5 DXB FTIR.

MONOMER SYNTHESIS

Methyl Urethane¹¹

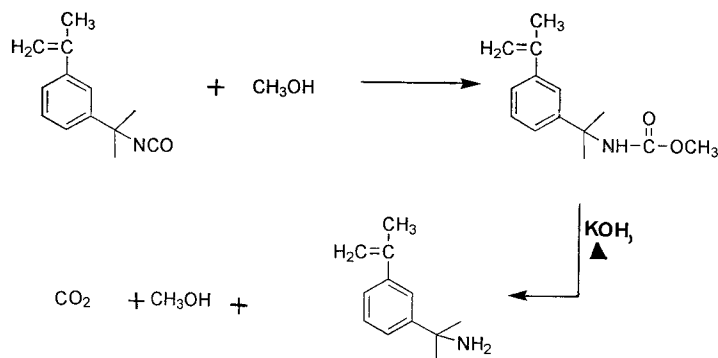
A 1-L flask equipped with a mechanical stirrer, reflux condenser, thermometer, and pressure-

equalizing addition funnel was charged with m-TMI (201 g, 1.0 mol) and dibutyltin dilaurate (0.8 g). Methanol (32 g, 1.0 mol) was charged to the addition funnel. The methanol was added dropwise to the vigorously stirred m-TMI over the course of 30 min. There is an exotherm during the methanol addition that increases the temperature of the flask contents by ~20°C. After all the methanol had been added, the exotherm was allowed to subside (15–20 min) and the reaction mixture was then heated at 60°C for 4 h. An infrared spectrum of the reaction mixture showed no —NCO absorbance (2270 cm⁻¹) at this point, so the reaction mixture was allowed to cool to ambient temperature. When ambient temperature was reached (22°C), the entire reaction mixture solidified. The solid was isolated by filtration and dried *in vacuo* (35°C) to a constant weight.

Yield = 96.3% ¹H-NMR, CDCl₃: δ = 7.51 (s, 1 H); δ = 7.29 (m, 3H); δ = 5.40 (b.s. 1H); δ = 5.38 (s, 1H); δ = 5.19 (s, 1H); δ = 3.55 (s, 3H); δ = 2.15 (s, 3H); δ = 1.63 (s, 6H).

IDBA

Methyl urethane (200 g, 0.86 mol) was dissolved in 200 g of butyl cellosolve[®] and this solution was added to a 2-L flask equipped with a mechanical stirrer, reflux condenser, and thermometer. A solution of KOH (85 g of 85%, 1.3 mol) in 350 g of



Scheme 1 Monomer synthesis.

Table II Copolymerization Results

Polymer	M_1^a	M_2	Mol Fraction M_1 in Feed	Polymerization Time (h)	Polymerization Temperature (°C)	Percent Conversion	Mol Fraction M_1 Polymer	M_n	M_w
AMST1	Styrene	IDBA	0.87	1.33	75	22.8	0.87	18,000	29,000
AMST2	Styrene	IDBA	0.84	1.33	75	18.0	0.83	15,000	24,000
AMST3	Styrene	IDBA	0.82	1.33	75	7.8	0.81	12,000	19,000
AMST4	Styrene	IDBA	0.80	1.33	75	5.0	0.80	8400	14,000
AMST5	Styrene	IDBA	0.78	1.33	75	12.0	0.77	7000	12,500
AMST6	Styrene	IDBA	0.76	1.33	75	9.1	0.74	5800	10,000
AMST7	Styrene	IDBA	0.68	1.33	75	9.5	0.65	3900	5500
AMST8	Styrene	IDBA	0.51	1.33	75	8.4	0.45	2800	4400
AMMA1	MMA	IDBA	0.92	1.75	75	10.6	0.89	1100	2000
AMMA2	MMA	IDBA	0.89	3.25	75	34.5	0.87	1300	2200
AMMA3	MMA	IDBA	0.87	3.25	75	33.7	0.83	2900	3300
AMMA4	MMA	IDBA	0.84	3.25	75	26.4	0.82	2400	3000
AMMA5	MMA	IDBA	0.76	4.00	75	14.9	0.72	2600	3400
AMMA6	MMA	IDBA	0.35	4.00	75	5.7	0.44	2700	3300
AMBM1	BMA	IDBA	0.87	1.75	75	9.6	0.87	8300	14,000
AMBM2	BMA	IDBA	0.63	5.00	75	11.0	0.68	2700	5900
AMBM3	BMA	IDBA	0.49	5.00	75	7.9	0.56	2400	3500
AMBM4	BMA	IDBA	0.46	5.00	75	7.3	0.54	1900	3900
AMVP1	4VP	IDBA	0.82	0.5	75	65.2	0.74	— ^b	—
AMVP2	4VP	IDBA	0.79	0.5	75	57.0	0.70	—	—
AMVP3	4VP	IDBA	0.63	0.5	75	21.2	0.53	—	—
AMVP4	4VP	IDBA	0.52	0.5	75	9.8	0.47	—	—
AMVP5	4VP	IDBA	0.43	0.5	75	8.6	0.45	—	—
AMVP6	4VP	IDBA	0.35	0.5	75	6.9	0.34	—	—

The values given are the average of two experiments performed at each feed composition.

^a MMA, methyl methacrylate; BMA, *n*-butyl methacrylate; 4VP, 4-vinylpyridine.

^b These copolymers apparently adhere to the inner walls of the GPC columns and do not pass the detector, so no molecular weights were obtained. However, viscosity measurements indicate molecular weights in the range of other copolymers synthesized for this study.

Butyl Cellosolve[®] was added and the reaction mixture was refluxed for 4 h. The reaction mixture was allowed to cool to ambient temperature and 250 mL of water followed by 350 mL of 1,2-dichloroethane was added. This mixture was stirred at ambient temperature for 12 h and was then poured into a separatory funnel. The organic layer was isolated, washed with water (2 × 300 mL), and then dried with anhydrous Na₂SO₄. The dichloroethane was removed under reduced pressure and the residue was subjected to vacuum-distillation. The IDBA had a boiling point of 90–93°C at 1.0 mm.

Yield = 78%. ¹H-NMR, CDCl₃: δ = 7.36 (d, 1H); δ = 7.25 (m, 3H); δ = 5.39 (s, 1H); δ = 5.05 (s, 1H); δ = 2.15 (s, 3H); δ = 1.59 (s, 2H); δ = 1.40 (s, 6H).

COPOLYMER SYNTHESIS

Reactivity Ratios

Copolymers for this part of the investigation were synthesized by weighing the desired quantity of each comonomer into a clean, dry, thick-walled vial. The initiator (AIBN, 1.0 wt %) was added and the vial contents were sparged with dry nitrogen while cold (evaporation loss ~0.3 wt %). The vials were tightly sealed with Teflon-lined screw caps and placed in a thermostated oil bath at the desired temperature. The vials were removed from the bath after an arbitrary time interval and the contents were allowed to cool to ambient temperature. Cold methanol or heptane was then added to the vial to precipitate the copolymer. The copolymers were purified by two

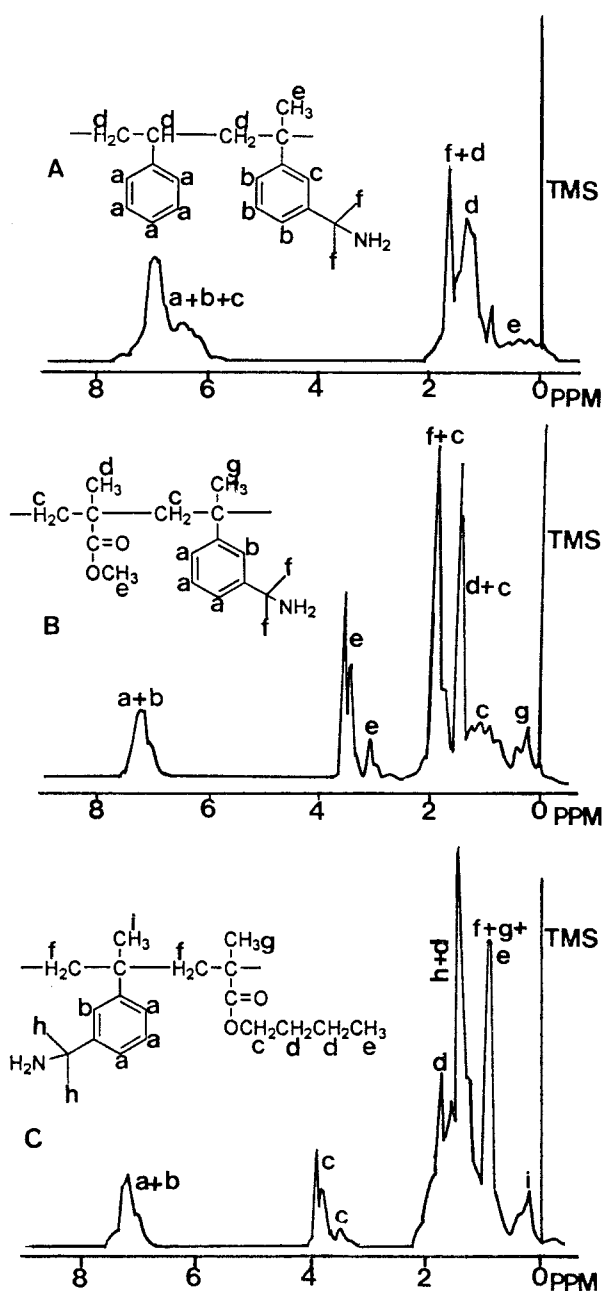


Figure 1 300-MHz $^1\text{H-NMR}$ spectra of (A) AMST4, (B) AMMA3, and (C) AMBM4.

reprecipitations from the CHCl_3 solution into either methanol or heptane. The copolymers were then dried *in vacuo* at 30°C to a constant weight. Conversions were determined gravimetrically.

Time-Conversion Copolymerizations

For these experiments, styrene and methyl methacrylate were chosen as the comonomers. Two different feed compositions for each comono-

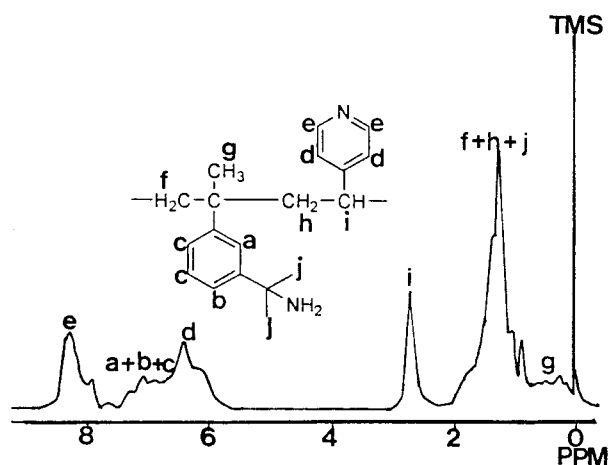


Figure 2 300-MHz $^1\text{H-NMR}$ spectrum of AMVP3.

mer were polymerized at two different temperatures. Vials were removed from the bath at intervals and the copolymer was isolated and purified as described above. Again, conversions were determined gravimetrically.

Film-evaluation Copolymers

In addition to evaluating some of the copolymers synthesized as described above in the films, copolymers containing styrene, IDBA, and lauryl methacrylate were synthesized. The lauryl methacrylate was added to lower the T_g of the polymer so better film formation could be obtained. The composition and some characterization data of these copolymers are presented in Table I.

Coating Solutions

The coating solutions used for making the films were prepared by dissolving 50 g of the copolymer in 50 g of methyl ethyl ketone, dividing this solution into two equal parts, and adding a stoichiometric amount of a crosslinking agent to one part. The other part would serve as the control. Films of both solutions were made by drawing aliquots over Bon-

Table III Reactivity Ratios

M_1	M_2	R_1	R_2
Styrene	IDBA	1.09	1.70
MMA	IDBA	0.63	0.38
BMA	IDBA	0.97	0.46
4VP	IDBA	0.36	0.50

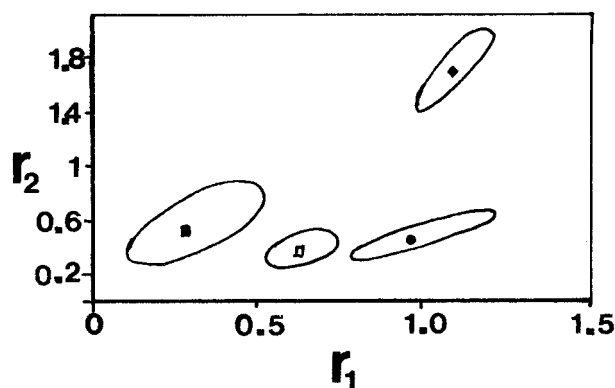


Figure 3 Joint confidence intervals: (◆) styrene/IDBA; (□) MMA/IDMA; (●) BMA/IDBA; (■) 4VP/IDBA.

drite 1000 steel panels with a #3 Bird bar (dry film thickness = 1.2–1.5 mil). The panels were then heated at 130°C in a forced-air oven for varying lengths of time. The panels were removed from the oven and cooled to ambient temperature and the films were evaluated for property development.

RESULTS AND DISCUSSION

A previously reported amine functional monomer, IDBA, was synthesized by a new route as shown

in Scheme 1. Using the route shown in Scheme 1, 74–80% overall yields of IDBA (average = 76%) were obtained. In contrast, Kania et al.'s procedure gave only 9–20% overall yields. The principal reason for the difference in yields seemed to be the quantity of side products formed. Kania's procedure gives large quantities of *m*-TMI-containing diaducts, while our method significantly reduces or eliminates such products.

Having established a method to synthesize IDBA in relatively high yields, we next investigated the polymerization behavior of IDBA. Several attempts, using various initiators (AIBN, BPO, Vazo 88), were made at homopolymerizing IDBA. All attempts failed. This is not a surprising result as IDBA is an α -methylstyrene-type monomer and it is well known that α -methylstyrene-type monomers do not homopolymerize under standard free-radical conditions.¹² However, it is equally well known that α -methylstyrene-type monomers readily copolymerize under free-radical conditions. Therefore, copolymerization of IDBA with various comonomers was attempted. We found that copolymerization did occur and the calculation of reactivity ratios was possible. The copolymerization data are summarized in Table II, and as copolymer compositions were deter-

Table IV Time—Conversion Results: Styrene/IDBA

Polymer	M_f of M_1 ^a Feed	Polymerization Temperature (°C)	Polymerization Time (min)	Conversion (wt %)	M_n	M_w
1	0.90	75	35	12.7	11,900	23,500
2	0.90	75	65	27.7	12,000	23,000
3	0.90	75	85	37.3	12,300	23,800
4	0.90	75	110	46.0	—	—
5	0.90	75	155	61.2	12,000	2400
6	0.80	75	30	7.8	3800	5500
7	0.80	75	60	15.2	2700	5100
8	0.80	75	90	26.9	5500	9500
9	0.80	75	120	36.0	5500	10,800
10	0.80	75	150	61.2	3700	8000
11	0.90	85	25	22.6	9100	17,200
12	0.90	85	63	52.1	10,000	18,600
13	0.90	85	83	60.1	9300	17,900
14	0.90	85	111	63.3	8700	17,600
15	0.90	85	140	79.0	9900	19,500
16	0.80	85	25	13.6	4200	7200
17	0.80	85	63	36.4	4300	9200
18	0.80	85	83	50.9	5200	10,800
19	0.80	85	111	59.7	5800	12,400
20	0.80	85	140	66.0	5000	12,900

^a M_1 , styrene; M_f , mol fraction.

Table V Time–Conversion Results: MMA/IDBA

Polymer	M_f of M_1^a Feed	Polymerization Temperature (°C)	Polymerization Time (min)	Conversion (wt %)	M_n	M_w
1	0.90	75	30	8.4	1100	1300
2	0.90	75	64	15.5	1000	1600
3	0.90	75	93	21.2	2200	4400
4	0.90	75	120	26.8	4200	9400
5	0.90	75	150	34.2	5200	11,500
6	0.80	75	30	5.1	1000	1400
7	0.80	75	64	9.6	—	—
8	0.80	75	93	13.5	2800	3700
9	0.80	75	120	18.4	2000	3600
10	0.80	75	150	23.2	2900	3900
11	0.90	85	30	11.4	4700	7300
12	0.90	85	60	23.9	4200	8900
13	0.90	85	80	33.0	5000	11,000
14	0.90	85	100	36.1	—	—
15	0.90	85	120	41.2	7000	12,200
16	0.80	85	30	11.0	2100	2700
17	0.80	85	60	19.9	2000	4300
18	0.80	85	80	22.5	2000	4100
19	0.80	85	100	25.6	3000	6000
20	0.80	85	120	36.0	4400	7100

^a M_1 , MMA.

mined by ¹H-NMR spectroscopy, several representative spectra are shown in Figures 1 and 2 (peak assignments are given in the figures^{13,14}).

The reactivity ratios were calculated using a nonlinear least-squares analysis.^{15–17} Specifically, the method used accounts for the conversions obtained.¹⁸ The values obtained for the reactivity ratios are listed in Table III. The joint confidence intervals are shown in Figure 3.

The values obtained for r_1 and r_2 show that IDBA readily copolymerizes, at least with vinyl aromatic and methacrylate comonomers. While the selection of comonomers is limited, there is no reason to believe that IDBA would not copolymerize well with other representatives of these industrially important classes of monomers. We chose not to attempt copolymerization with acrylate monomers at the time this study was done because of the possibility of the occurrence of the Michael reaction between the amine functionality of IDBA and the double bond of the acrylate.¹⁸ While the reaction might be slow due to the steric bulk of the amine, it could still be a complicating side reaction. However, IDBA–acrylate copolymerizations will be the subject of future investigations.

Because manufacture of IDBA copolymers was a distinct possibility, we needed to have a general

idea of the time–conversion profiles of these copolymerizations. So, we chose two comonomer pairs, styrene–IDBA and MMA–IDBA, and performed copolymerizations at two different temperatures and at two different feed ratios. The data that we obtained are listed in Tables IV and V and plotted in Figures 4 and 5.

The time–conversion results show the expected trend. At higher temperature, higher rates of polymerization result. The data also show that the feed concentration of IDBA affects the rate of copolymerization; in general, higher feed levels of IDBA slow the rate of copolymerization. The rate of copolymerization is greater for styrene–IDBA than for MMA–IDBA. Most likely, this is due to steric compression from the α -methyl groups of both MMA and IDBA. Higher levels of IDBA in the feed results in lower molecular weight products. This is not surprising as the lower rate of copolymerization at higher IDBA levels give more time for side reactions such as chain transfer to occur.

The amine functional copolymers were used to formulate coating compositions which were made into thermoset films by crosslinking. The crosslinkers used were the epoxy functional species shown in Figure 6. The properties of the films obtained are summarized in Table VI.

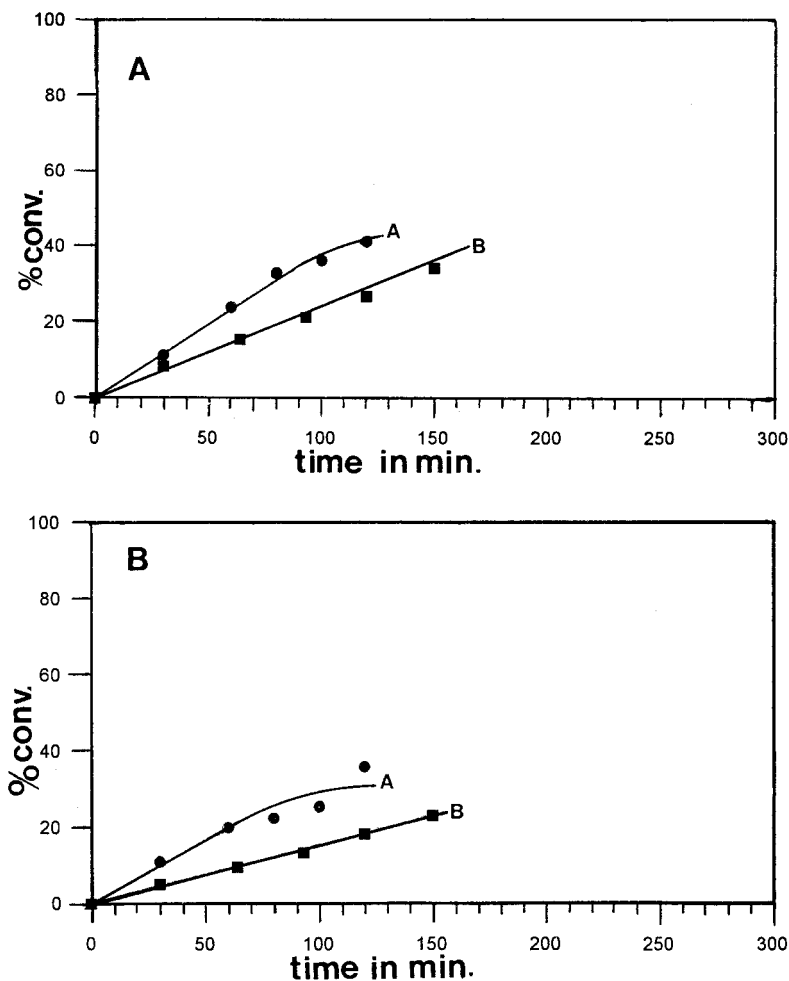


Figure 4 Time-conversion plots: (A) MMA/IDBA, 90/10, A = 85°C, B = 75°C; (B) 80/20, A = 85°C, B = 75°C.

The controls used for the film-evaluation study were the IDBA-containing copolymers without an added crosslinker. In all controls, films with one to three MEK double rubs were obtained. The film test results show that the cure of IDBA-containing copolymers is relatively slow. Long reaction times (~12 h) are necessary to achieve a high degree of solvent resistance. Even lower molecular weight epoxies (ECEC) do not produce highly resistant films in reasonable bake times. However, the films produced do show some property development in as little as 30 min with some of the crosslinking agents used. This is particularly true for the copolymers containing higher levels of IDBA (Polymer 1 from Table I). As it is known that bisphenol A (Bis A)-type epoxies react more readily with amines than do cycloaliphatic or aliphatic epoxies,¹⁹ IDBA copolymers might be cured more effectively with Bis-A types of epoxies.

This possibility is currently under investigation in these laboratories.

CONCLUSIONS

A new higher yield synthesis was developed for a previously reported monomer, 3-IBDA. The current synthetic route produces 2.5–3.5 times the yield of the previous procedure. We found that IDBA did not homopolymerize under free-radical initiation conditions, but readily copolymerized with styrene- and methacrylate-type monomers. The IDBA proved most reactive in copolymerization with styrene, with nearly equal reactivity ratios being obtained. While the variety of comonomers investigated was limited, two of the three most important classes of addition polymerization monomers, vinyls and methacrylates,

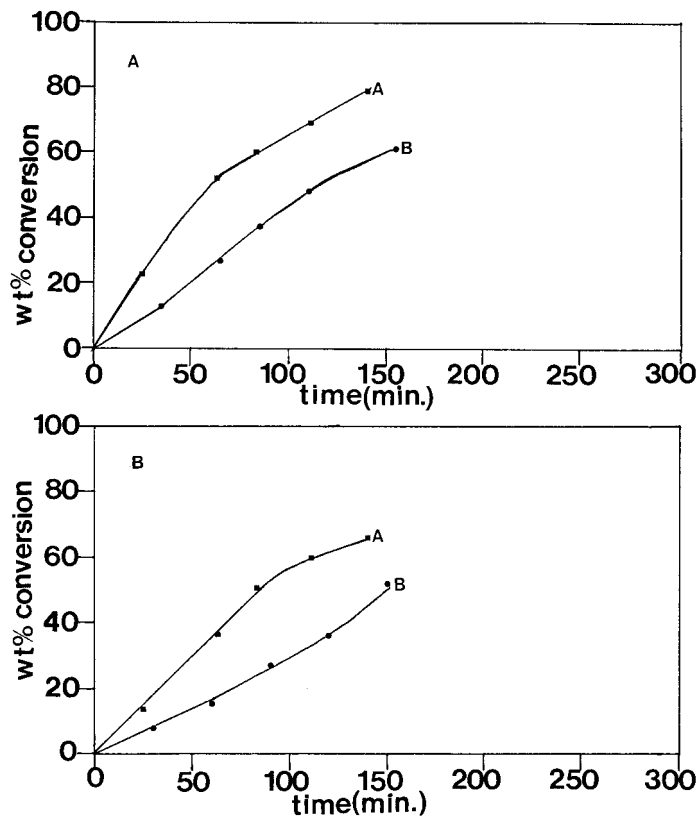


Figure 5 Time-conversion plots: (A) styrene/IDBA, 90/10, A = 85°C, B = 75°C; (B) 80/20, A = 85°C, B = 75°C.

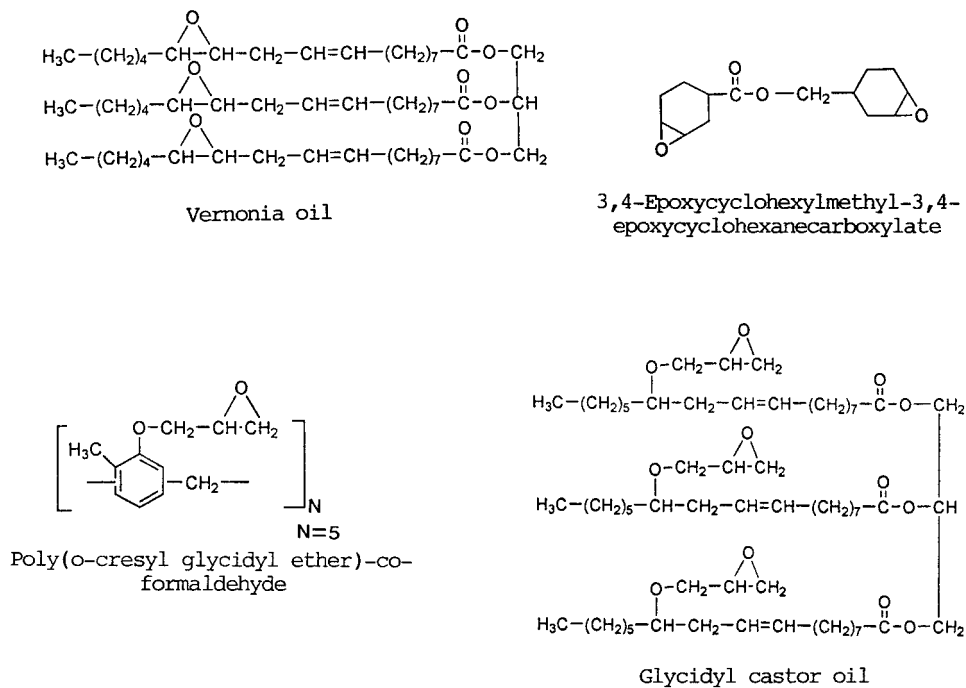


Figure 6 Epoxy functional crosslinkers.

Table VI Coating Results

Film No.	Polymer ^a	Crosslinker ^b	Bake Temperature (°C)	Bake Time (min)	MEK Double Rubs ^c	Pencil Hardness	Forward Impact ^c (in lbs)	60° Gloss
1	1	V.O.	130	30	120	HB	50	91
2	1	V.O.	130	60	130	H	40	90
3	1	V.O.	130	90	139	H	40	93
4	1	V.O.	130	120	150	2H	20	89
5	1	V.O.	130	720	260	3H	10	94
6	1	GCO	130	30	37	HB	60	93
7	1	GCO	130	60	50	F	50	85
8	1	GCO	130	120	70	H	30	65
9	1	GCO	130	180	180	2H	20	70
10	1	CGEF	130	30	40	HB	60	91
11	1	CGEF	130	60	50	H	40	89
12	1	CGEF	130	120	70	2H	30	84
13	1	CGEF	130	180	100	2H	30	80
14	1	ECEC	130	30	60	H	30	85
15	1	ECEC	130	60	80	H	30	93
16	1	ECEC	130	90	105	2H	10	92
17	2	CGEF	130	30	30	B	60	92
18	2	CGEF	130	60	39	HB	60	90
19	2	CGEF	130	120	48	H	25	92
20	2	CGEF	130	180	60	H	25	88
21	2	V.O.	130	30	10	B	100	93
22	2	V.O.	130	60	45	HB	80	92
23	2	V.O.	130	120	60	HB	70	94
24	2	V.O.	130	360	90	H	40	92
25	2	ECEC	130	30	45	H	40	80
26	2	ECEC	130	60	50	H	40	96
27	2	ECEC	130	90	70	2H	20	95
28	3	ECEC	130	30	10	B	80	94
29	3	ECEC	130	45	15	B	80	92
30	3	ECEC	130	60	22	B	70	92
31	3	GCO	130	30	9	B	90	93
32	3	GCO	130	60	15	B	80	94
33	3	GCO	130	120	24	HB	60	89
34	3	GCO	130	180	30	HB	60	93
35	3	CGEF	130	30	10	B	80	95
36	3	CGEF	130	60	13	B	80	95
37	3	CGEF	130	120	18	B	80	90
38	3	CGEF	130	180	28	HB	50	88

^a Polymer 1: polymer 1 from Table I; polymer 2: polymer 2 from Table I; polymer 3: polymer 3 from Table I.

^b V.O., Vernonia oil; GCO, glycidyl castor oil; CGEF, poly[(*o*-cresylglycidylether)-*co*-formaldehyde]; ECEC, 3,4-epoxy cyclohexyl methyl-3,4-epoxycyclohexanecarboxylate.

were represented. The number of points collected in each copolymerization data set is also limited in some cases. While this may affect the absolute accuracy of the reactivity ratio values reported, the general trend shown by the values reported is believed to be correct, that is, there is some tendency toward alternation, except for the styrene copolymers. This is expected because of the limited homopolymerization ability of IDBA.

Larger-scale copolymerizations, with different levels of IDBA, were conducted to obtain sufficient material for film studies to be performed. Lauryl methacrylate was used in the synthesis of these polymers so that materials with lower T_g 's could be obtained, which we hoped would result in films with better forward and reverse impact resistance. Unfortunately, by the time crosslinking had proceeded to a relatively low level, as mea-

sured by methyl ethyl ketone resistance, the forward impact resistance became fairly low (as did the reverse impact resistance). This result is not totally unexpected as acrylic and styrene-acrylic films are not noted for flexibility. Copolymers with higher levels of IDBA incorporation produced films with better properties (in terms of solvent resistance) in shorter periods of exposure to elevated temperature. However, long bake times were required to obtain films with very high solvent resistance (250+ methyl ethyl ketone double rubs). A different type of crosslinker might improve this situation.

The time-conversion studies showed that good yields of copolymers could be obtained in reasonable amounts of time if the feed level of IDBA is not too high. The feed level of IDBA not only affects the reaction rate but also influences the molecular weight of the copolymer produced with generally lower molecular weights produced at higher feed concentrations of IDBA. It seems that mol percents of IDBA in the feed should be 15–20% for optimum reaction rates, molecular weights, and cure behavior.

The experiments conducted in this work did not address lower VOC issues directly. However, the primary aim of this work was the evaluation of the IDBA monomer in copolymerization reactions and evaluation of the resulting copolymers in film applications. The IDBA proved to be reasonably reactive in copolymerization reactions. The copolymers were curable with epoxy functional species. The use of IDBA in low VOC systems is a current topic of investigation in our laboratories.

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