

# Synthesis of Acrylic Resins for High-Solids Coatings by Solution and Separation Polymerization

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## INTRODUCTION

The goal of this study was to find conditions under which oligomeric acrylic polyol resins with low polydispersity ( $D = M_w/M_n$ ) and relatively low viscosity can be synthesized using an economical free radical polymerization process for use as resins in high-solids coatings. Low polydispersity is desired because it facilitates formulation of high-solids coatings—the lower the polydispersity at a given  $M_n$ , the higher the solids, other factors being equal. Acrylic oligomers for high-solids coatings often have number average molecular weights ( $M_n$ ) of 1000–3000 (around 7–27 monomer units per chain) and polydispersities on the order of 1.7 to 2.1.<sup>1,2</sup>

Two processes were studied: conventional solution polymerization under monomer-starved conditions<sup>3</sup> and a modified process. In the modified process, polymerization was performed under monomer-starved conditions in aliphatic or cycloaliphatic solvents that are good solvents for the monomers but poor solvents for the products. We call the modified process *separation polymerization*, because the polymer, or oligomer, separates as it forms. It is similar to *precipitation polymerization* except that the polymer separates as a viscous liquid, not as a precipitate. The product often solidifies when it cools to room temperature.

Nine potential advantages of separation polymerization are described in the Discussion Section. Not all were demonstrated in this study, but we found that the process offers a convenient way to prepare acrylic polyol resins at high (>90%) solids. The resins can then be dissolved in any combination of solvents desired in the paint formulation. We speculate that the process reduces the likelihood that any solvent residues attached to polymers by chain transfer are less likely to adversely affect weatherability than residues of polar solvents, such as ketones.<sup>4</sup>

Two monomer line-ups were investigated: one is composed of methyl methacrylate (MMA), butyl acrylate (BA), styrene (Sty), and poly (ethylene glycol) methacry-

*Conventional solution polymerization under monomer-starved conditions was compared with separation polymerization, also known as monomer-starved, as a method for making acrylic resins with low polydispersity ( $D=M_w/M_n$ ). Separation polymerization employs aliphatic or cycloaliphatic solvents that are good solvents for the monomers but poor solvents for the resin; thus, the resin separates during polymerization. Various process conditions, initiators, chain-transfer agents, and solvents were studied, focusing mainly on a monomer line-up of methyl methacrylate, styrene, ethyl acrylate, and 2-hydroxyethyl methacrylate in a 15/15/40/30 weight ratio. Two initiators, t-amyl peroxy 2-ethyl hexanoate and t-butyl peroxy 2-ethyl hexanoate gave about equal, excellent results. 2-Mercapto ethanol was selected as a chain transfer agent. With these ingredients, the separation polymerization method is capable of producing oligomeric acrylic polyol resins with polydispersities (D) of about 1.7 to 1.8 when  $M_n$  is in the range 1350 to 1600. These resins have substantially lower solution viscosities than a commercial benchmark resin, which has  $M_n=1230$  and  $D=2.03$ . In preliminary tests of 2K polyurethane coatings, the film properties obtained with acrylics made by separation polymerization were, on balance, superior to those obtained with a commercial benchmark resin.*

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Table 1—Polymerization Parameters and GPC Results of Series A Resins

Acrylic Resins	Wt% <sup>(a)</sup> Initiator	Wt% Chain Transfer Agent	Polymerization T (°C) Solvent	Wt% Solvent	Product State	M <sub>n</sub>	M <sub>w</sub>	M <sub>p</sub>	D	NVM (%)
A1	10 TAPH	5 ME	105 propyl acetate	75	Solution	909	2927	2852	3.22	22
A2	10 TAPH	5 ME	110 toluene	75	Solution	1087	2692	2556	2.48	24
A3	10 TAPH	5 ME	135 xylene	75	Solution	636	1441	1310	2.26	23
A4	10 TAPH	5 ME	105 propyl acetate	75	Solution	993	3700	3067	3.72	22
A5	10 TBPH	5 ME	135 xylene	75	Solution	631	1444	1310	2.29	24
A6	10 TRB	5 ME	135 xylene	75	Solution	865	2170	1883	2.50	23
A7	10 V67	5 ME	135 xylene	75	Solution	521	1160	1068	2.22	23
A8	15 TAPH	15 ME	135 xylene	25	Solution	461	1182	999	2.56	22
A9 <sup>(b)</sup>	15 TAPH	15 ME	135 xylene	25	Solution	461	1137	942	2.60	22
A10	7 TAPH	0 ME	135 xylene	40	Solution	2385	13331	4970	5.58	71
A11	7 TAPH	4 ME	135 xylene	40	Solution	1253	5586	4142	4.46	71
A12	10 TAPH	5 ME	135 xylene	40	Solution	988	2532	2736	3.57	70
A13	3 TAPH	5 ME	135 xylene	40	Solution	1387	9330	5008	6.73	70
A14	2 TAPH	10 ME	135 xylene	40	Solution	2048	15383	1364	2.56	90 <sup>(c)</sup>
A15	2 TAPH	1 ME	175 Mineral spirits	25	ssps <sup>d</sup>	608	15383	4191	7.5	90 <sup>(c)</sup>
A16	3 TAPH	3 ME	175 Mineral spirits	25	ssps	2083	10605	3829	5.09	91
A17	3 TAPH	5 ME	175 Mineral spirits	25	ssps	1912	6336	3388	3.31	90
A18	3 TAPH	8 ME	175 Mineral spirits	25	ssps	1741	5675	3198	3.26	90
A19	3 TAPH	10 ME	175 Mineral spirits	25	ssps	1708	5218	3287	3.04	90
A20	3 TAPH	12 ME	175 Mineral spirits	25	ssps	1511	4765	2834	3.03	90

(a) The wt% of initiator, chain transfer agent and solvent are based on the total monomer weight.

(b) Addition time: 3.5 hr.

(c) The NVM of resins A15 through A20 were directly determined after the solvent layer was poured off the acrylic resins.

(d) The symbol "ssps" means semi-solids phase separated with a solvent layer on the resin.

late (PEGMA). This is believed to impart outstanding mar resistance to coatings (see Results Section). The other is composed of methyl methacrylate (MMA), ethyl acrylate (EA), styrene (Sty), and 2-(hydroxyethyl) methacrylate (HEMA), a line-up expected to provide an economical oligomer that would impart to coatings a good overall balance of properties.

## EXPERIMENTAL

### Materials

**MONOMERS, CHAIN TRANSFER AGENTS, AND INITIATORS:** Methyl methacrylate (99%), butyl acrylate (99%), styrene (Sty) (99%), poly(ethylene glycol)methacrylate ( $M_n = 526$ ), ethyl acrylate (99%), 2-(hydroxyethyl) methacrylate (97%), 2-mercaptoethanol (ME) (98%), octanethiol (OC), and dodecanthiol (DO) were obtained from the Aldrich Chemical Co. *t*-Amyl peroxy 2-ethyl hexanoate (TAPH) (95%) and *t*-butyl peroxy 2-ethyl hexanoate (TBPH) (95%) were provided by Aztec Chemical Co.; *bis*(1,1-dimethylethyl)peroxide (Trigonox<sup>®</sup>-B, TRB) was obtained from Akzo Nobel Co.; and 2,2'-azobis(2-methylbutyronitrile) (Vazo<sup>®</sup> 67, V67) was obtained from Aldrich Chemical Co.

**SOLVENTS AND REACTION MEDIA:** Mineral spirits (bp = 179–210°C), xylene (bp = 135°C), toluene (bp = 110°C), and propyl acetate (bp = 105°C) were obtained from the Aldrich Chemical Co. and were used as supplied. Isopar<sup>®</sup>-E (bp = 118–140°C), Isopar<sup>®</sup>-G (bp = 160–177°C), and SC<sup>®</sup>-100 (bp = 160°C) were obtained from Exxon Chemical Co. Cypar<sup>®</sup>-7 (bp = 97–105°C) and Cypar<sup>®</sup>-9 (bp = 138–168°C) were obtained from Shell Chemical Co. For convenience, these materials are all called "solvents" in this paper.

**CROSSLINKERS, BENCHMARK RESIN, SURFACE TENSION MODIFIER AND CATALYST:** Polyisocyanates: Desmodur N-3300, an isocyanurate of 1,6-hexamethylene diisocyanate (HDI-ICU), and Desmodur Z-4470 BA, an isocyanurate of isophorone diisocyanate (IPDI-ICU) were obtained from Bayer Corp. The commercial benchmark resin, "Joncryl 920," an acrylic polyol supplied at 80% NVM in a methyl amyl ketone (MAK) solution, was obtained from SC Johnson. All these materials were used as received. Fluorad<sup>®</sup> (FC-430) obtained from the 3M and dibutyltin dilaurate (DBTDL) obtained from the Aldrich Chemical Co. were diluted to 20% and 10%, respectively, solutions in MAK before use. Fluorad<sup>®</sup> FC-430 is thought to be a partially fluorinated hydrocarbon; it serves as a surface tension modifier.

Test panels were 3 × 6" cold-rolled steel panels with a dull matte finish, Q-Panel number R-36.

### Synthesis of Acrylic Resins

**GENERAL PROCEDURE:** A 250-mL round-bottom flask equipped with a mechanical stirrer, a thermometer with a temperature controller, an N<sub>2</sub> inlet, a Graham condenser equipped with a cold finger using ice water as the cold trap, a dropping funnel and a heating mantle was charged with half of the total amount of the solvent

to be used and heated to reflux or to the desired temperature. In certain experiments, a similarly equipped 500-mL flask was used. A solution of mixed monomers, initiator, chain transfer agent, and the second half of the solvent was added dropwise into the flask over a period of 1.0 or 3.5 hr with stirring and heating at the desired reaction temperature. After addition was complete, an additional 10% of the amount of the initiator initially used for the polymerization was added, and the temperature was maintained for another 1.0 hr. When aliphatic or cycloaliphatic hydrocarbons were used as the solvents, phase separation was discernable when stirring was rapid during the reaction process and was obvious when the stirring speed was reduced. The proportions of reactants, the amount and type of solvent, and the reaction temperature for each oligomer are shown in *Tables 1* and *2*. The product solution or mixture was poured into a pre-weighed container and was cooled to room temperature. The acrylic resin was obtained as a solution, a solvent-swollen (ss) semi-solid, or a semi-solid phase separated (ssps) depending upon the type and amount of solvent. The yield was >98%. Solids content (NVM) was measured by ASTM D 2369. When the resin was obtained with two distinctly separated phases (ssps), the upper layer was decanted, and NVM of the lower layer was measured.

Series A resins were synthesized with proportions by weight of monomers: MMA/Sty/BA/PEGMA = 12/13/31/44. Different initiators (TAPH, TBPH, TRB, and V67) and different solvents (propyl acetate, toluene, xylene, and mineral spirits) were employed in various amounts. (See *Table 1* for details.)

Series B resins were synthesized with proportions by weight of monomers MMA/Sty/EA/HEMA = 15/15/40/30. Different initiators (TAPH or TBPH), solvents (xylene, mineral spirits, Cypar-9, Cypar-7, the Isopar-E and -G, and SC-100), and chain transfer agents [2-mercaptoethanol (ME), octanethiol (OC), and dodecanethiol (DO)] were studied. (See *Table 2*.)

**EXAMPLE: SYNTHESIS OF RESIN A17:** A 250-mL round-bottom flask equipped as described in the general procedure was charged with 7.2 g of mineral spirits (boiling point 175°C) and heated to reflux. A solution of 7.2 g of MMA, 7.8 g of Sty, 18.6 g of BA, 26.4 g of PEGMA, 1.8 g of TAPH, 3.0 g of 2-mercaptoethanol, and 7.5 g of mineral spirits was added over a period of one hour under a slow stream of N<sub>2</sub>. During the process of the addition of the monomer mixture, the temperature was maintained at 175 ± 2°C. Phase separation became visible after about 10% of the monomer mixture had been added and became evident as the reaction progressed. When addition was complete another 0.18 g of TAPH was added, and refluxing was continued for one hour. The product mixture was poured into a weighed container and left to cool to room temperature. The acrylic resin separated as a white semi-solid. The upper, solvent-rich, layer was poured off; NVM of the bottom layer was 90%.

**EXAMPLE: SYNTHESIS OF RESIN B6:** A 250-mL round-bottom flask equipped as described in the general procedure was charged with 15 g of mineral spirits and heated to 150°C. A solution of 9.1 g of MMA, 9.1 g of Sty, 24.2 g of EA, 18.5 g of HEMA, 1.9 g of TAPH, 3.1 g of 2-

mercaptoethanol, and 15 g of mineral spirits was added over a period of one hour under a slow stream of N<sub>2</sub>. During the process of the addition of the monomer mixture, the temperature was maintained at 150 ± 2°C. Phase separation became visible after about 10% of the monomer mixture had been added and became evident as the reaction progressed. Another 0.19 g of TAPH was added at once, and refluxing was continued for one hour. The product mixture was poured into a weighed container and left to cool to room temperature. The acrylic resin separated as a white semi-solid. The upper, solvent-rich, layer was poured off; NVM of the bottom layer was 92%. Analysis of the two layers by gas chromatography showed unreacted monomer content was 0.2 wt% in the resin layer and 0.15 wt% in the solvent layer.

### Characterization of Resins

Gel permeation chromatography (GPC) analyses were carried out with a Hewlett Packard 1050 series Liquid Chromatograph with an HP 1047A differential refractometer as the detector. THF was used as a solvent at a flow rate of 0.9 mL/min through a series of three Phenogel® columns (pore size: 10<sup>5</sup>, 10<sup>3</sup>, 10<sup>2</sup>Å). During the study, the columns wore out and were replaced with new ones. Nine-point polystyrene calibration standards were used with the old columns and 13-point polystyrene standards were used with the new ones. Comparisons with selected resins showed that the old and new columns and calibration procedures gave the same M<sub>n</sub> values within experimental error; the new columns gave slightly lower M<sub>w</sub>/M<sub>n</sub> values with the same resin.

Gas chromatography (GC) analysis of silylated samples was performed using a Hewlett-Packard 5809A Gas Chromatograph with a flame ionization detector. Silylated 1,4-butanediol was used as an internal standard. The silylating agent was an 80/20 w/w mixture of hexamethyldisilazane and N,O-bis(trimethylsilyl)-trifluoroacetamide.

Samples of acrylic resins for differential scanning calorimetry (DSC) were dissolved in MAK, concentrated in a rotary evaporator at 70°C for five hours at water aspirator pressure and then kept in an oven for five days at 70°C under vacuum. DSC was performed on the same resins with two instruments: (1) a Seiko DSC-220CU; samples were heated with a heating rate of 30°C/min from 30° to 150°C, and maintained at that temperature for three minutes to delete thermal history, then quenched to -40°C, followed by re-heating at 20°C/min to 150°C, and (2) a TA Instruments Model 2100 modulated DSC with scanning from -60°C to 100°C at 5°C/min.

Viscosity of acrylic resins was determined using a Brookfield DV-II+ viscometer at 25°C with a #31 spindle rotating at 3 rpm. Non-volatile by mass (NVM) was determined by ASTM D 2369-95. The hydroxyl values of the acrylic resins were determined according to ASTM D 1957-86.

### Preparation of Clearcoats

Series B acrylic resins obtained as ssps were concentrated in a rotary evaporator at 70°C for five hours at

water aspirator pressure to reduce volatile content below 1 wt%. The residual resins were dissolved in MAK. In certain instances, NVM was adjusted to 80%, and viscosity was measured. MAK solutions of these resins were combined with polyisocyanates HDI-ICU and/or IPDI-ICU, using a 1.1/1 NCO/–OH equivalent ratio (a 1.1:1 index), and FC-430 (0.25 wt% of total weight of the acrylic resin and polyisocyanate on a solids basis) were prepared at room temperature in a 50-mL beaker. Viscosity and NVM of the resulting solutions were measured; NVM was 80 to 90%. Just before application, dibutyltin dilaurate (0.05 wt% of the total weight of acrylic resin and polyisocyanate on total solids) was mixed thoroughly into the solution. Coatings with thicknesses of about 50  $\mu\text{m}$  were prepared by casting the above solution on steel panels using a #34 drawdown rod. Some coatings were dried at ambient temperature for 96 hr, and other coatings were baked at 120°C for 30 min. Baked panels were kept at ambient temperature for one day before testing. Clearcoats made from Joncryl 920 and HDI-ICU and/or IPDI-ICU (1.1/1 of –NCO/–OH) were also prepared by this procedure and used as the benchmark.

### Characterization of Clearcoats

Viscosity of clearcoats was determined using a Brookfield DV-II+ viscometer at 25°C with a #31 spindle rotating at 3 rpm. The NVM was determined by ASTM D 2369-95. Film thickness was measured with a Microtest® magnetic thickness gauge. The pencil hardness and both direct (DIR) or reverse (REV) impact resistance was measured according to ASTM D 3364 and D 2794 methods, respectively. Elongation tests were performed on a mandrel tester according to ASTM D 522-93a. Methyl ethyl ketone (MEK) resistance was tested by double rubbing with MEK saturated nonwoven paper ("Kim-wipe™"); the nonwoven paper was kept saturated by MEK during the measurement; results were recorded as the smallest number of rubs that would expose bare metal of the panel. Adhesion was tested according to ASTM D 3359-95a.

## RESULTS

### Synthesis and Characterization of Series A Acrylic Resins

This study started with evaluation of different conditions for polymerization of Series A resins, made from the monomers MMA/Sty/BA/PEGMA in a 12/13/31/44 wt% ratio. This monomer combination was chosen because preliminary experiments indicated that resins with this composition impart outstanding mar resistance to coatings crosslinked with melamine-formaldehyde or polyisocyanate crosslinkers. Their exceptional mar resistance is attributed to the presence of a flexible spacer separating the crosslink site from the resin backbone, in accordance with previously reported results.<sup>5</sup> The focus of this report is the effect of polymerization conditions on molecular weight and on polydispersity index, ( $D=M_w/M_n$ ). The effects of amount and types of solvents, initiators, and chain transfer agents on the mo-

lecular weight and molecular weight distribution were studied. The results are shown in *Table 1*.

Resins A1-A14 were synthesized in propyl acetate, toluene, or xylene, good solvents for the product, while Resins A15–A20 were synthesized in mineral spirits, a solvent for the monomers but not for the products. As expected from well-known theories,<sup>6</sup>  $M_n$  of the resins decreased as initiator and chain transfer agent levels increased. Polydispersity index (D) ranged from 2.3 to 7.5, suggesting that side reactions, perhaps chain transfer to poly(ethylene oxide) groups of the oligomer, increased D. There were indications that separation polymerization yields lower D than solution polymerization. For example, Resins A17 and A20, produced by separation polymerization, had a lower D than comparable Resin A13, made by solution polymerization. It is true that solution polymerized resins had relatively low D, but only when  $M_n$  was below about 1000. Separation polymerization seemed to give lower D than solution polymerization when  $M_n$  was about 2000. Xylene, which has the highest reflux temperature among solution polymerization solvents, produced the narrowest molecular weight distribution.

The  $M_n$  and D of resins A3, A5, A6, and A7, made with initiators TAPH, TBPH, TRB, and V67, respectively, indicated that comparable resins can be obtained by using TAPH, TBPH, or V67, but that TRB causes higher molecular weight and broader molecular weight distribution. Initiators TAPH, TBPH, and V67 have similar one-hour half-time temperatures of 85°, 84°, and 90°C, respectively, while TRB has higher one-hour half-time temperature of 136°C.<sup>7</sup> Resins A8 and A9, in which the feed time was 1.0 and 3.5 hr, respectively, had similar molecular weight and D, suggesting that the more rapid processing has little influence on the product, at least when working on this small scale. Comparison of resins A3 ( $D = 1441/636; 2.26$ ) and A12 ( $D = 2532/988; 3.57$ ) suggest that variations in the amount of solvent may make a substantial difference.

### Synthesis and Characterization of Series B Acrylic Resins

The effect of process variables on synthesis of a more conventional monomer line-up for high-solids coatings was then studied. Series B acrylic resins were based on the monomer line-up: MMA/Sty/EA/HEMA = 15/15/40/30 (wt. ratio), in which HEMA serves as the functional monomer. *Table 2* summarizes the results.

All the acrylic resins synthesized from this monomer line-up show significantly lower polydispersities than resins of Series A synthesized under similar conditions. When aliphatic or cycloaliphatic solvents were used, the Series B acrylic resins separate as a white semi-solid with a non-volatile content of 90% or more.

The effects of several process variables were studied:

**MONOMER FEED RATE:** Resins B1 and B2 have essentially identical  $M_n$  and D. The only difference between these runs was monomer addition time, 3.5 hr for B1 and 1.0 hr for B2. This result supports the conclusion from Series A—that this much variation in feed rate has negligible effect. Therefore, in runs B3–B33 the monomer was added in one hour.

Table 2—Polymerization Parameters and GPC Results of Series B Resins

Acrylic Resins	Wt% <sup>a</sup> Initiator	Wt% Chain Transfer Agent	Polymerization T (°C) Solvent	Wt% Solvent	Product State	M <sub>n</sub>	M <sub>w</sub>	M <sub>p</sub>	D	NVM (%)
B1 <sup>b</sup>	3 TAPH	10 ME	175 Mineral spirits	25	ssps <sup>d</sup>	728	1300	1192	1.78	92
B2	3 TAPH	10 ME	175 Mineral spirits	25	ssps	738	1283	1188	1.74	91
B3	3 TAPH	10 ME	175 Mineral spirits	50	ssps	759	1314	1221	1.73	91
B4	3 TAPH	10 ME	150 Mineral spirits	50	ssps	796	1340	1264	1.68	91
B5	3 TAPH	5 ME	175 Mineral spirits	50	ssps	1319	2540	2452	1.92	92
B6	3 TAPH	5 ME	150 Mineral spirits	50	ssps	1349	2532	2439	1.87	92
B7	3 TAPH	5 ME+DO	150 Mineral spirits	25	ssps	1730	3897	3068	2.25	91
B8	3 TAPH	10 ME	120 Mineral spirits	50	ssps	847	1465	1384	1.73	92
B9	3 TAPH	5 DO	150 Mineral spirits	50	ssps	2705	7641	4455	2.82	92
B10	3 TAPH	5 OC	150 Mineral spirits	50	ssps	2177	5661	4106	2.60	91
B11	3 TAPH	5 ME	120 Mineral spirits	50	ssps	1466	2780	2647	1.89	91
B12	3 TAPH	6 DO	150 Mineral spirits	50	ssps	2182	6743	3992	3.09	91
B13	3 TAPH	10 DO	175 Mineral spirits	25	ssps	1424	3166	2485	2.22	92
B14	3 TAPH	10 ME+DO	150 Mineral spirits	50	ssps	1120	1970	1870	1.76	92
B15	3 TAPH	10 ME	135 Xylene	50	solution	844	1441	1375	1.71	67
B16	3 TAPH	5 ME	135 Xylene	25	solution	816	1383	1310	1.69	82
B17	3 TAPH	5 ME	135 Xylene	50	solution	1522	2854	2757	1.87	72
B18	3 TAPH	3 ME	135 Xylene	25	solution	2146	4412	4173	2.05	90
B19	3 TAPH	5 ME	115 Isopar <sup>®</sup> -E	50	ss <sup>e</sup>	1711	4772	3546	2.78	79
B20	3 TAPH	5 ME	160 Isopar <sup>®</sup> -G	50	ss	1187	2370	2356	1.99	82
B21	3 TAPH	5 ME	160 Isopar <sup>®</sup> -G	10	ss	1288	2600	2400	2.02	82
B22	3 TAPH	5 ME	142 Cypar <sup>®</sup> -C9	50	ssps	1391	2674	2592	1.92	91
B23	3 TAPH	5 ME	104 Cypar <sup>®</sup> -C7	50	ss	1439	3119	2734	2.16	80
B24	3 TAPH	5 ME	160 SC <sup>®</sup> -100	50	ssps	1043	2040	1926	1.95	91
B25	3 TAPH	4 ME	142 Cypar <sup>®</sup> -C9	10	ssps	1768	3414	3206	1.93	97
B26	3 TAPH	3 ME	142 Cypar <sup>®</sup> -C9	10	ss	2086	4324	4043	2.07	97
B27	2 TAPH	5.4 ME	142 Cypar <sup>®</sup> -C9	10	ssps	1693	3533	3400	2.08	97
B28	3 TAPH	3 ME	142 Cypar <sup>®</sup> -C9	50	ssps	2293	4255	3961	1.85	90
B29	3 TAPH	5 ME	145 Mineral spirits	50	ssps	1541	2673	2532	1.73	90
B30	3 TAPH	5 ME	145 Mineral spirits	50	ssps	1640	2783	2611	1.70	90
B31	3 TBPH	5 ME	145 Mineral spirits	50	ssps	1523	2629	2474	1.73	90
B32	4.5 TBPH	5 ME	145 Mineral spirits	50	ssps	1129	2126	1987	1.88	90
B33	5.5 TBPH	5 ME	145 Mineral spirits	50	ssps	1172	2174	2002	1.86	90

(c) The wt% of initiator, chain transfer agent and solvent are based on the total monomer weight.

(b) Addition time: 3.5 hr.

(c) The NVM of the ssps resins were directly determined after the acrylic resins were separated from solvent.

(d) The symbol "ssps" means semi-solid phase separated with a solvent layer on the resin.

(e) The symbol "ss" means solvent-swollen.

(f) Repeated experiments.

**Table 3—Viscosity of Selected Acrylic Resins in Comparison with their Molecular Weight and Molecular Weight Distribution**

Acrylic Resins	$M_n$	$M_w$	$M_z$	D	Viscosity (mPa.s, 25 ± 1°C, 3 rpm, 80% NVM in MEK)
B1 .....	728	1300	2043	1.78	1045
B13 .....	1424	3166	6818	2.22	7039
B14 .....	1120	1970	2941	1.76	2907
B6 .....	1349	2532	3898	1.87	4011
B11 .....	1466	2780	4329	1.89	4212
B22 .....	1391	2674	4127	1.92	4229
B29 .....	1541	2673	4060	1.73	4059
B31 .....	1523	2629	3970	1.73	4339
B32 .....	1129	2126	3400	1.88	3655
Benchmark <sup>a</sup> .....	1233	2498	4160	2.03	6047

(a) Joncryl J-920

**INITIATOR TYPE AND CONCENTRATION:** Based on the results of Series A, 3 wt% of TAPH was used in most of the experiments in Series B. For comparison, TBPB was used in runs B31–B33. There was no detectable difference between the initiators—compare runs B29 and B30 (replicas) with B31.

The initiator concentration was varied in runs B31–B33. As predicted by polymerization theory<sup>6</sup> and expected from common experience, increasing initiator concentration decreases  $M_n$ , although the difference between products B32 and B33 was small.

**CHAIN TRANSFER AGENT CONCENTRATION AND TYPE:** Gray<sup>8</sup> showed that hydroxy functional mercaptan chain transfer agents effectively control the molecular weight of acrylic oligomers. Comparison of runs B3 with B5, of B8 with B11, and of B15 with B17 show similar effects in our process. 1-Dodecanethiol, 1-octanethiol and 2-mercaptoethanol were used in B9, B10 and B6; the differences in  $M_n$  of the products can be attributed to differences in the molecular weights of the chain transfer agents. Functional chain transfer agents, such as 2-mercaptoethanol were used in this study because they may improve film mechanical properties<sup>8,9</sup> and despite their potential adverse effect on weatherability<sup>10</sup> (see Discussion Section). Of course,  $M_n$  and  $M_w$  increase as concentrations of initiator and chain transfer agent are reduced.<sup>6</sup> In most experiments, as  $M_n$  and  $M_w$  increase, D also increases to a modest extent.

**POLYMERIZATION TEMPERATURE:** Since most of the experiments were performed in refluxing solvent, it is difficult to unequivocally separate the effect of solvent composition from that of reaction temperature. Comparison of runs B6, B16, and B19–B24 suggest that lower polymerization temperatures give higher  $M_n$  and perhaps higher D, consistent with the results from Series A. The most directly comparable resins, B3, B4, and B8, suggest that decreasing polymerization temperature increases  $M_n$  but has little effect on D.

A concern about reaction temperature was the fact that these polymerizations were effected at temperatures above the boiling points of one (MMA bp = 100°C) or more (styrene bp = 144°C) of the monomers. In general, oligomer yields were 98% or higher, indicating minimal loss of these monomers by evaporation. Only about 0.2% of unreacted monomers remain in the product. Use of an efficient reflux condenser, a slow nitrogen flow, and the monomer-starved conditions are sufficient to minimize monomer losses.

**TYPE AND AMOUNT OF SOLVENT:** Perusal of the data in Table 2 suggests that there is little difference between the polydispersities (D) produced by solution polymerization and separation polymerization. For example, with a particular composition, solution polymerization in xylene (run B16–B18) gave D of 1.69 (at  $M_n$  = 8200) to 2.05 (at  $M_n$  = 2150) while separation polymerizations (runs B20–B24 and B29–B31) gave D in the range 1.70 to 2.16. Generally, D increases as  $M_n$  increases, but note that separation polymerized resins B30 and B31 have D = 1.70 – 1.73, at  $M_n$  = 1540 – 1640, while the commercial benchmark resin has D = 2.02 at  $M_n$  = 1230.

The data in Table 2 suggest that solvents used for separation polymerization can be ranked for value in yielding low D in approximately the following order: Mineral spirits ~ Cypar-9 > SC-100 > Isopar-G > Cypar-7 > Isopar-E. Minimum D produced in these solvents is 1.87, 1.92, 1.95, 2.02, 2.16, and 2.78, respectively.

It is difficult to discern a clear-cut pattern relating boiling points or compositions of these solvents to their performance in reducing D. Mineral spirits are rich in isoparaffins, while Cypar-9 contains 99% cycloparaffins. These two solvents appear to be attractive choices for further research on separation polymerization.

In separation polymerization experiments, the amount of solvent was varied from 10 to 50%. This change appears to have little (compare B26 with B28) or no (compare B20 with B21) influence on  $M_n$  and D of the products. The solvent level also seemed to have little influence on D of the products of solution polymerization; direct comparisons of  $M_n$  are not possible.

**UNREACTED MONOMERS:** To determine the free monomer content in the acrylic polyols synthesized with either mineral spirits or Cypar-9 as the solvent, we ran GC/MS experiments for acrylic resin B6 with phase separation of the upper layer (phase rich in solvent) and the bottom layer (phase rich in resin), and acrylic resin B26 without phase separation (solvent-swollen) because only 10 wt% solvent was used. For acrylic resin B6, the bottom layer contains 129 µg/g of MMA, 926 µg/g of EA, and 599 µg/g of HEMA; Sty could not be measured due to peak overlap with the solvent (MAK) used to dissolve the resin. The total weight of the free monomers in the acrylic polyol's mass does not exceed 2000 µg/g, which means that the acrylic resin contains less than 0.20 wt% of free monomers. The mineral spirits upper layer contains 704 µg/g of MMA, 449 µg/g of EA, and 339 µg/g Sty; no HEMA was detected. Absence of HEMA was

confirmed by measurement of the -OH number of the upper layer as zero. Thus, the upper layer decanted from resin B6 contained 0.15% free monomers. Acrylic resin B26, from which no solvent was decanted, contains 689  $\mu\text{g/g}$  of MMA, 2665  $\mu\text{g/g}$  EA, 300  $\mu\text{g/g}$  HEMA, and 640  $\mu\text{g/g}$  of Sty for a total of 0.42 % free monomers.

**SOLVENT RECYCLE:** The possibility of reusing the solvent-rich layer, which can be readily separated from the acrylic resins, was investigated. The mineral spirits-rich layer decanted from resin B6 was used to prepare another batch of B6 under the same. About 10% of fresh mineral spirits was added to replace losses. The  $M_n$  and  $D$  of the product were 1467 and 2.04, respectively, compared to 1349 and 1.87 for the product made with fresh mineral spirits. Multiple experiments would be needed to determine whether repeated use of recycled mineral spirits degrades the product.

### Viscosities and Glass Transition Temperatures of Series B Acrylic Resins

The viscosity and glass transition temperature ( $T_g$ ) of selected resins made by separation polymerization was compared to the benchmark resin and to a resin of similar composition made by solution polymerization in xylene. To make valid comparisons, it is necessary to equalize the solvent type and level and, for  $T_g$  studies, the recent solvent history of the resins. Solvent was decanted from the acrylic resins made by separation polymerization, and the volatile content of the resins was reduced to < 1% by concentrating them in a rotary evaporator at 70°C for five hours under water aspirator pressure. For viscosity studies, the NVM was adjusted to 80% by adding MAK to obtain a homogeneous solution. The benchmark resin was used as received; it is already at 80% NVM in MAK. Viscosity and molecular weight data are summarized in *Table 3*.

When molecular weights were similar, our acrylic resins with  $D < 2.0$  had 28 to 52% lower viscosity than "Joncryl 920" at the same solids content. An indication

of the great sensitivity of viscosity to  $D$  is shown by comparing resin B13 ( $M_n = 1424$ ,  $D = 2.22$ ) with other resins, for example B29 ( $M_n = 1541$ ,  $D = 1.73$ ); viscosity of B13 is 73% higher. This result confirms the importance of minimizing  $D$  for high-solids coatings. Another aspect of this result is that  $M_w$  (3166) and  $M_z$  (6818) of B13 are higher than  $M_w$  (2673) and  $M_z$  (4060) of B29.

Differential scanning calorimetry (DSC) was performed on two instruments. The  $T_g$  of resin B6 was +5°C (Seiko) and +1°C (TA), while  $T_g$  of the benchmark resin was -3°C (Seiko) and -6°C (TA). These results show that  $T_g$  of resin B6 is about 7 to 8°C higher than that of the benchmark resin and rules out the possibility that the lower viscosity of the experimental resins can be explained by  $T_g$  effects.

### Clear Coatings Made from Series B Acrylic Resins

A preliminary study of high-solids coatings made from Series B acrylic resins was carried out, and results were compared with coatings made from Joncryl 920. These coatings were two-package (two-component, 2K) acrylic polyurethanes designed for air dry or moderate bake applications. Three acrylic resins were studied, B30, in which the initiator was TAPH, B31, a similar resin made with TBPH as the initiator, the benchmark resin. The crosslinkers were hexamethylene diisocyanate homopolymer (HDI-ICU), and isophorone diisocyanate homopolymer (IPDI-ICU). Other factors being equal, films made from HDI-ICU will be considerably softer and more flexible than films made from IPDI-ICU because HDI has a flexible, aliphatic structure while IPDI has a relatively rigid, cycloaliphatic structure. It is common in industry to blend these crosslinkers to achieve the desired balance of hardness and flexibility.

Properties of clearcoats made from these resins and crosslinkers are shown in *Tables 4* through 7. Viscosity of these formulations (without catalyst) was adjusted to 0.1 Pa.s by addition of MAK and NVM was measured. As

**Table 4—Formulations and Properties of Clearcoat**

Air-Dried Clearcoats				
Acrylic polyol (Initiator)	B30 TAPH	B31 TBPH	B31 TBPH	Commercial Benchmark
-OH number	165	165	165	140
DBTDL (wt%)	0.05	0.05	0.05	0.05
FC-430(wt%)	0.25	0.25	0.25	0.25
-NCO/-OH equiv. ratio	1.1/1	1.1/1	1.1/1	1.1/1
NVM (%)	80	80	90	80
Wt% solvent at 0.1 Pa.s	20%	20.3%	—	21.4%
Film thickness (mils)	1.4-1.8	1.8-2.0	1.8-2.0	1.6-1.8
MEK resistance, dbl. rubs	>200	>200	>200	165
Pencil hardness	HB	HB	HB	HB
Adhesion	4B	4B	4B	1B
Impact resistance (Dir/Rev)	160/160	160/160	160/160	160/160
Elongation (%)	>32	>32	>32	>32
Baked Clearcoats (120°C for 30 min)				
MEK resistance, dbl. rubs	>200	>200	>200	165
Pencil hardness	H	H	H	4B
Adhesion	0B	1B	1B	0B
Impact resistance (Dir/Rev)	60/0	80/40	80/40	0/0
Elongation (%)	0 <sup>a</sup>	>32	>32	0 <sup>a</sup>

(a) The film delaminated during testing (HDI-ICU Crosslinker).

**Table 5—Coatings Properties of Clearcoats**

Air-Dried Clearcoats			
Acrylic polyol (Initiator) .....	B30 (TAPH)	B31 (TBPH)	Commercial Benchmark
Film thickness (mils) .....	1.7-1.9	1.8-1.9	1.6-1.8
MEK resistance, dbl. rubs .....	40	50	>200
Pencil hardness .....	F	F	HB
Adhesion .....	5B	5B	1B
Impact resistance (Dir/Rev) .....	20/20	20/20	0/0
Elongation (%) .....	>32	>32	0 <sup>a</sup>
Baked Clearcoats (120°C for 30 min)			
MEK resistance, dbl. rubs .....	>200	>200	>200
Pencil hardness .....	6H	6H	HB
Adhesion .....	3B	3B	0B
Impact resistance (Dir/Rev) .....	0/0	0/0	0/0
Elongation (%) .....	Cracked at 32	Cracked at 32	Cracked at 32

(a) The film delaminated during testing (IPDI-ICU Crosslinker; Formulations essentially the same as in Table 4.)

expected from their lower viscosity, formulations based on B30 and B31 had higher solids, but the difference was much smaller than the differences in resin viscosity. Even at 90% NVM, coatings made from resin B31 had sufficiently low viscosity that they could easily be cast on panels. Film mechanical properties of the clearcoats made from B30 and B31 were closely similar. Their properties were equal, and in some respects better than those of coatings made from the benchmark resin. Evaluations were made on matte cold-rolled steel panels, a substrate to which some of acrylic coatings tend to have poor adhesion. In general, adhesion of coatings made from B30 and B31 was equal to or better than those made from the benchmark resin. Part of the poor performance of the benchmark coatings in physical tests may result from poor adhesion. As expected, properties ranging from soft and flexible to hard and brittle are accessible by using HDI-ICU (Table 4) or IPDI-ICU (Table 5.) The data in Tables 6 and 7 illustrate the intermediate properties attainable by using blends of these crosslinkers.

## DISCUSSION

Intensive research has been underway for many years to find ways to synthesize acrylic polymers and copolymers with polydispersity much lower ( $D = 1.2$  or less) than is attainable by conventional free-radical polymerization (theoretical lower limit is  $D = 1.5$ ). Processes that have achieved some degree of laboratory success have included anionic polymerization,<sup>11</sup> group transfer polymerization,<sup>12</sup> mediated living free-radical polymerization,<sup>13,14</sup> atom transfer radical polymerization,<sup>15</sup> and many variations of these methods. These methods give low polydispersity because they have different kinetic characteristics than conventional radical initiated polymerization—the rate of propagation is slower than the rate of initiation, while with unmediated radical polymerization, the rate of propagation is much faster than the rate of initiation. However, none of the newer methods has yet proved capable of economically producing functional acrylic copolymers, such as oligomeric polyols. Thus, for the foreseeable future, the coatings industry will probably rely on unmediated free-radical polymerization for

production of most of its acrylic polyols, and the goal of obtaining the lowest possible  $D$  remains an important one.

There are conflicting reports in the literature about which initiators can be expected to give acrylic resins with the lowest polydispersity. Kamath and Sargent reported that *t*-amyl peroxides give lower polydispersity than *t*-butyl counterparts.<sup>16</sup> This result is supported by theoretical expectations, since *t*-amyl peroxides decompose to produce ethyl, rather

than methyl, radicals as the initiating species, and the less reactive ethyl radicals are, in theory, less likely to cause side reactions such as branching. More recently, Myers published data, obtained under different conditions, indicating that the two types of initiators give about the same polydispersity.<sup>17</sup> In our experiments, the two initiators performed the same within experimental error in both Series A and Series B. In Series A, 2,2'-azobis(2-methylbutyronitrile) also performed similarly, while *bis*(1,1-dimethylethyl) peroxide gave broader polydispersities. Factors such as initiation rate, cost, toxicity, availability, and probable effect on weatherability are also involved in the selection of initiators.

Polymerization theory predicts a linear decrease in  $M_n$  as chain transfer agent molar concentration increases for cases where the reactivity of the chain transfer agent is relatively high.<sup>6</sup> Gray confirmed this theory for synthesis of acrylic oligomers using a variety of functional mercaptan chain transfer agents,<sup>8</sup> and our results fit the same pattern. For most experiments 2-mercaptoethanol was chosen because it effectively controls molecular weight and it has an additional advantage: it introduces a hydroxyl functional group on the end of each chain it initiates. Theoretical calculations predict that use of 2-mercaptoethanol will substantially decrease the population of chains in the acrylic resin that have less than two hydroxyl groups.<sup>9</sup> In theory, this should improve film mechanical properties, although there may be adverse effects on weatherability whenever mercaptan chain transfer agents are used.<sup>10</sup>

In 80% solutions in MAK, the viscosities of Series B resins are 28 to 52% lower than the benchmark commercial resin. The difference cannot be explained by  $T_g$  effects, since  $T_g$  of resin B6 is actually 7 to 8°C higher than that of the benchmark resin. Remaining possibilities are the lower polydispersities of the B Series resins, differences in branching levels, or some unexplained structural or solvent-interaction differences. Further research would be needed to explain this difference. It seems almost certain that reduced polydispersity helps reduce resin viscosity. When clearcoats are formulated from resin B6 and the benchmark resin, the viscosity differences are much smaller. The fact that these resins have



lower viscosity than the benchmark resin despite having higher  $M_n$  and  $T_g$  suggests that factors other than  $T_g$ ,  $M_n$ , and  $D$  may have a strong influence on viscosity. These factors probably include differences in oligomer structure, but additional study would be needed to establish what the specific differences are.

Perusal of the data in Table 3 suggests that, for Series B resins having  $M_n$  between 1100 and 1600, there is a good correlation of viscosity with  $M_w$  and  $M_z$ . The benchmark resin, of course, does not correlate with the Series B resins, having a much higher viscosity than expected for its molecular weight. As indicated previously, differences in  $T_g$  cannot account for this difference. Presumably, differences in resin structure explain it; the effect of such differences would be an interesting topic for further investigation.

The solution and separation polymerization processes both gave resins having polydispersity ( $D$ ) of about 1.7. However, solution polymerization gave  $D$  as low as 1.7 only when  $M_n$  was 800–850 (resins B15–B16); it gave  $D = 1.87$  when  $M_n$  was 1520 (resin B17). In contrast, separation polymerization gave  $D = 1.70 - 1.73$  when  $M_n$  was 1520–1640 (resins B30 and B31). Thus, it may prove an attractive alternative to solution or bulk polymerization.

With separation polymerization, polymer characteristics are essentially the same whether the process is performed at 50 or 90 wt% solids. At 50 wt%, most of the solvent separates as an upper layer, which can be easily removed and potentially recycled. At 90 wt% no solvent layer separates. Either way, a concentrated product containing 10 wt% or less of aliphatic or cycloaliphatic solvent is obtained. It can be made pumpable by mild heating. Residual aliphatic or cycloaliphatic solvent can be removed by vacuum stripping before dilution or simply left in the product. Removal of the solvent layer also removes about half the unreacted monomer, and there is a possibility that it could also remove other undesirable contaminants.

At the outset of this study, we envisaged potential advantages of the separation polymerization process in comparison with conventional solution polymerization methods: (1) resins can be produced at very high solids, (>90%) while

60% is about the maximum with solution polymerization, (2) the resins can be dissolved in different solvents or solvent mixtures depending on what coating production and application characteristics are required, (3) the aliphatic solvents used in separation polymerization can be recycled, (4) if desired, resins synthesized by separation polymerization can be shipped in concentrated form, (5) separation polymerization is very easily controlled, and modest variations in polymerization temperature and the amount of solvent seem to have little affect on the structure and properties of the final resins, (6) the solvents used in the new method are less expensive than xylene and oxygenated solvents, (7) polymerization can be effected in solvents which are less likely than aromatic or oxygenated solvents to undergo side reactions such as chain transfer or transesterification; it is speculated that this may be advantageous for weatherability, (8) when the aliphatic solvent layer is decanted, it may take with it a small fraction of undesired components of the resin, such as unreacted monomer and low-molecular weight, non-functional oligomers, a potential advantage for film mechanical properties and weatherability, and (9) separation of the polymer during polymerization may minimize side reactions such as chain transfer

**Table 6—Coatings Properties of Clearcoats**

Air-Dried Clearcoats			
	B30 (TAPH)	B31 (TBPH)	Commercial Benchmark
Acrylic polyol (Initiator)	B30 (TAPH)	B31 (TBPH)	Commercial Benchmark
Film thickness (mils)	1.6-1.8	1.8-2.0	1.6-1.8
MEK resistance, dbl. rubs	>200	>200	>200
Pencil hardness	B	B	HB
Adhesion	4B	4B	0B
Impact resistance (Dir/Rev)	80/80	80/80	5/5
Elongation (%)	>32	>32	0 <sup>a</sup>
Baked Clearcoats (120°C for 30 min)			
MEK resistance, dbl. rubs	>200	>200	>200
Pencil hardness	H	H	B
Adhesion	5B	5B	0B
Impact resistance (Dir/Rev)	60/40	60/40	0/0
Elongation (%)	0 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>

(Mixed HDI-ICU/IPDI-ICU Crosslinkers, Equivalent ratio: 3/1; Formulations essentially the same as in Table 4.)  
 (a) The film delaminated during testing.

**Table 7—Properties of Clearcoats**

Air-Dried Clearcoats			
	B30 (TAPH)	B31 (TBPH)	Commercial Benchmark
Acrylic polyol (Initiator)	B30 (TAPH)	B31 (TBPH)	Commercial Benchmark
Film thickness (mils)	1.7-1.8	1.8-1.9	1.6-1.8
MEK resistance, dbl. rubs	>200	>200	>200
Pencil hardness	F	F	HB
Adhesion	5B	5B	0B
Impact resistance (Dir/Rev)	60/40	60/40	0/5
Elongation (%)	>32	>32	0 <sup>a</sup>
Baked Clearcoats (120°C for 30 min)			
MEK resistance, dbl. rubs	>200	>200	>200
Pencil hardness	2H	2H	B
Adhesion	5B	5B	0B
Impact resistance (Dir/Rev)	10/0	10/0	0/0
Elongation (%)	0 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>

(Mixed HDI-ICU/IPDI-ICU Crosslinkers, Equivalent ratio: 1/1; Formulations essentially the same as in Table 4.)  
 (a) The film delaminated during testing.

to polymer. Of these potential advantages, 1-6 were demonstrated in this study, but 7-9 remain speculative.

Having established a process, it is a simple matter to adjust oligomer characteristics.  $M_n$  can be adjusted by altering the level of initiator and chain transfer agent; presumably the chain transfer agent could be eliminated, if desired, for a particular application.  $T_g$  and the hydroxyl number can be adjusted in predictable ways by changing the proportions of monomers. Thus, it is possible to adjust the final coating properties through a wide range to target specific requirements. Versatility is further enhanced by the possibility of using mixed crosslinkers. The hydroxyl equivalent weight of oligomers B30 is 340 g/equiv., while the hydroxyl equivalent weight of the benchmark is 400 g/equiv. This important factor, which affects both coating film properties and economics, can be equalized simply by changing the monomer proportions.

## CONCLUSIONS

This study has shown that both conventional solution polymerization and separation polymerization are capable of producing oligomeric acrylic polyol resins with polydispersities ( $D$ ) of about 1.7 with the monomer line-up used in Series B. Only separation polymerization produces such a low polydispersity when  $M_n$  is about 1600. Resins made by separation polymerization have substantially lower solution viscosities than the commercial benchmark acrylic resin, which has  $M_n = 1230$  and  $D = 2.03$ . In preliminary tests, the best of the Series B resins gave coating film properties that were, on balance, superior to those obtained with the benchmark resin. Resin characteristics such as  $T_g$  and  $M_n$  can be easily adjusted by changing the monomer line-up. Thus, the primary goal of the project has been achieved.

It is widely accepted that  $T_g$ ,  $M_n$ , and polydispersity ( $D$ ) have a substantial effect on the viscosity of acrylic oligomers in concentrated solution. The data in this study show that additional factors are also at work, and may have substantial influence on viscosity. These factors are probably related to the detailed structure of the oligomers, but at this stage we can only speculate as to what they may be.

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