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## POLYMERIC ACID FOR THIN FILM APPLICATIONS

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### ABSTRACT

Propyl and butyl half esters of the alternating copolymer isobutylene/maleic anhydride (IB/MAn) are polymers of high acid content (4.67 and 4.38 milliequivalent acid/g polymer). These polymers exhibit good physical performance in thin films, such as absence of cracking and minimal curl. The anhydride ring of the copolymer IB/MAn is opened in refluxing alcohol at atmospheric or elevated pressure; conversion is monitored by an IR probe (1783 vs. 1733  $\text{cm}^{-1}$ ). The polymers are stable up to about 50°C. Weight loss corresponding to the reversion to the anhydride structure is observed at higher temperature, with concurrent increase of anhydride resonances in the IR. Thermal stability of the half esters is similar to that of alkyl half esters of the alternating copolymers ethylene/maleic anhydride (EMA) and methyl vinyl ether/maleic anhydride (Gantrez<sup>®</sup> AN 119). The 1-propanol solution of the propyl half ester of IB/MAn copolymer is a shear thinning fluid, a significant advantage when coating at high speeds.

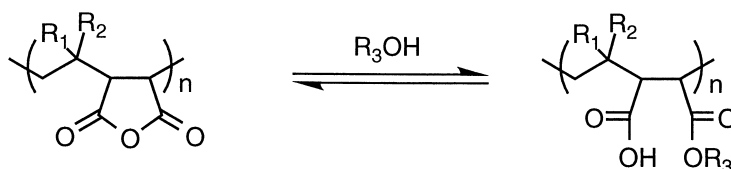
*Key Words:* Isobutylene/maleic anhydride copolymer; Maleic anhydride; Butyl ester; Propyl ester; Polymeric acid; Thin film; Cracking; Curl; Thermal stability; Rheology; Shear thinning

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## INTRODUCTION

Maleic anhydride copolymers are useful for the introduction of functional groups or crosslinking sites by polymer analog reactions. The anhydride group can be readily opened by reaction with an amine or alcohol, forming an amide or ester, respectively. Additional functional groups or polymer side chains can be attached to the polymer chain by the amine or alcohol, or crosslinks can be formed. The chemical scheme below shows an example for reaction with alcohols.  $R_1$  and  $R_2$  are  $-\text{CH}_3$  for IB/MAn, H for EMA,  $R_1$  is H and  $R_2$  is phenyl for styrene/MAn copolymer, and  $R_1$  is H and  $R_2$  is  $-\text{OCH}_3$  for methyl vinyl ether/maleic anhydride copolymer.  $R_3$  may carry additional functional groups.



*Scheme 1.*

Reactions with simple, normal alkyl alcohols provide some insight to the esterification process and typical polymer properties. In addition, the *n*-alkyl half esters are of practical importance. These are polymers with relatively high acid content and sufficient flexibility so that they are resistant to cracking and curl in thin, coated films. Industrial application of the methyl [1–9], ethyl [10] and butyl [11] half esters of the isobutylene/maleic anhydride copolymer is well documented in the patent literature, however, we found no publications in referenced journals. Surprisingly, no patent or publication was found on the 1-propyl derivative. Reported uses of the alkyl half esters of IB/MAn include adhesives, high-solids coating materials, polymeric foam applications, heat-resistant plastics, printing plates, etc.

## EXPERIMENTAL

### Synthesis

The IB/MAn alternating copolymer is dispersed in the corresponding alcohol (1-propanol or 1-butanol), the mixture is heated to reflux temperature, then refluxed for several hours. As the esterification progresses, the polymer slowly becomes swollen in the boiling alcohol, passes through a swollen gel state, and then gradually dissolves. When the reaction nears completion, the hazy, fine dispersion becomes a clear and colorless solution. Reaction conditions and analytical data on the polymers are summarized in Table 1. Due to the limited choice of common solvents that dissolve the



POLYMERIC ACID

Table 1. Synthesis and Analysis of IBMA Alkyl Half Esters

Exp. Number	Isobam Grade	Alcohol	Reaction Temp. (°C)	Reaction Time (hr)	Agitation (rpm)	Solids (wt%)	Viscosity (cPs)	Density (g/cm <sup>3</sup> )	Acid Cont. (meq/g)
1	6	1-BuOH	118	9	175	25.77	412		4.6
2	6	1-PrOH	97	10	175	28.37	492		5.44
3	6	1-PrOH	97	13	175	28.06	466	0.8867	4.95
4	6	1-PrOH	97	13	175	27.66	444	0.8830	4.98
5	6	1-PrOH	120	6	150	27.05	397	0.8829	4.74
6	6	1-PrOH	120	6	150	32.63	715	0.8979	4.94
7	6	1-PrOH	120	6	150	31.92	830	0.8970	4.95
8	6	1-PrOH	120	6	75	32.08	960	0.8979	5.03
9	6	1-PrOH	120	6	300	32.16	868	0.8987	4.96
10	4	1-PrOH	97	14	175	40.12	2285	0.9218	5.05
11	4	1-PrOH	120	6	150	32.24	540	0.8960	4.87
12	4	1-PrOH	120	6	150	32.07	499	0.8964	4.93
13	4	1-PrOH + H <sub>2</sub> O	120	6	150	32.24	574	0.8994	4.79
14	4	1-PrOH	117	6	150	32.12	463	0.8974	4.83
15	4	1-PrOH	123	6	150	32.30	436	0.9018	4.68
16	10	1-PrOH	120	6	150	30.13	2218	0.8894	4.80
17	10	1-PrOH	120	6	150	30.31	2340	0.8891	5.01
18	10	1-PrOH	120	6.5	140	30.39	2572	0.8899	4.82
19	10	1-PrOH	120	6.5	140	29.87	2460	0.8877	4.73
20	10	1-PrOH	120	6.5	140	30.52	3210	0.8903	4.48
21	10	1-PrOH	120	6.5	140	31.30	3425	0.8918	4.53
22	10	1-PrOH	120	6.5	140	31.09	2970	0.8917	4.52
23	10	1-PrOH	120	6.5	140	30.63	3270	0.8924	4.54



IB/MAn copolymers (dimethylformamide and dimethylsulfoxide), esterification in solution was not practical. Esterification with branched alcohols, such as 2-propanol, was very slow, probably due to steric hindrance. Neither of these avenues was further pursued in our current investigations.

Various molecular weight grades of the alternating copolymer IB/MAn, supplied under the trade name Isobam by Kuraray Co., are used in our experiments, the grade is also indicated in Table 1. The reaction proceeds at higher rates at higher temperatures, therefore the majority of the experiments are conducted at elevated pressures and temperatures. At elevated pressures (about 25 psi pressure is reached by heating the 1-propanol dispersion in an air-tight reactor to 120°C) the synthesis is performed in a stainless steel reactor (Mettler RC-1, Hastalloy pressure vessel). The conversion in the stainless steel reactor is monitored with an IR probe (ReactIR 1000 from ASI Applied Systems), comparing the IR absorbance at 1783  $\text{cm}^{-1}$  (anhydride resonance) and 1733  $\text{cm}^{-1}$  (ester resonance) as a function of reaction time. Typical curves for experiments 10 and 11 are shown in Fig. 1, which also illustrates relative reaction rates at reflux versus at 120°C under about 25 psi pressure. The intensities of the IR resonances simultaneously increase at the onset of esterification, when polymer dissolution makes IR detection possible. The intensity (peak height, relative to the baseline) of the acid and ester resonances for the carbonyl stretching vibrations continues to increase, while that of the anhydride resonance decreases with increasing conversion, until both reach a plateau. After heating is discontinued at 6 and 14 hours,

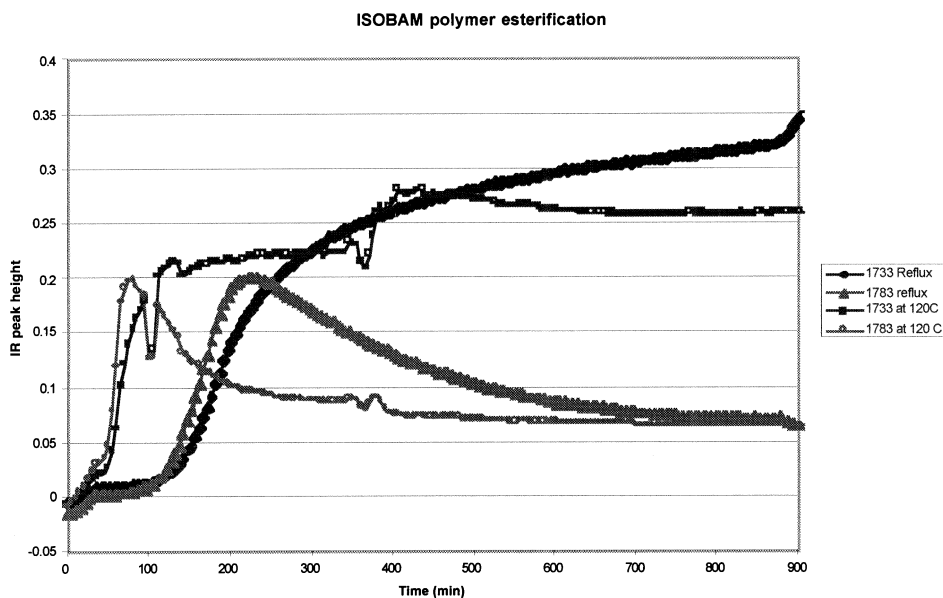


Figure 1. Isovam polymer esterification.



respectively, further small changes occur due to changes in volume/concentration as the temperature decreases. The initial experiments were conducted at atmospheric pressure (experiments 1–4 and 10). Close to complete conversion is reached in about 9 hours in 1-butanol (reflux temperature 118°C), as indicated by the acid value approaching the theoretical value, 4.38 milliequivalent acid/g polymer. In 1-propanol (reflux temperature 97°C) reaction time is about 13–14 hours (theoretical meq: 4.67 milliequivalent acid/g polymer). At elevated temperature, 120°C, conversion even with 1-propanol was practically complete in 6 hours, as indicated in Fig. 1. Our further experimentation focused on the 1-propyl half ester, since it has a clear practical advantage over the 1-butyl half ester. That is, the polymer can be directly coated from 1-propanol, while the boiling point of 1-butanol is too high to be completely removed in a typical coating operation.

Slight variations in reaction temperature had a negligible influence on final conversion at constant 6 h reaction time (experiments 14 and 15 compared to 11 and 12). A small amount of added water (0.2% on total weight, or 6.9 mol% on anhydride content) did not have any detectable effect on the acid content of the polymer (experiment 13 compared to 11 and 12). Significant changes in agitation rate had negligible effect on conversion or polymer properties (experiments 8 and 9 compared to 6 and 7).

Batch-to-batch reproducibility under identical reaction conditions was good (experiments 3 and 4, 6 and 7, 11 and 12, 16 and 17). Reproducibility was equally good in 30 kg size reactor (Hastalloy pressure vessel, experiments 18–23), where reaction time was increased to 6.5 hours. This brought the acid content of the copolymer even closer to the theoretical value (average of acid content of these experiments was 4.60 meq/g).

## RESULTS AND DISCUSSION

Polymer concentration or solid content, shown in Table 1, was determined by drying the samples until constant weight is reached in a vacuum oven at room temperature. Determination of solid content by drying the polymer solution in a hot oven for an extended time gives misleading results. The equilibrium, shown in Scheme 1, is pushed to the left at high temperatures in the absence of alcohol (dry polymer), and the half ester reverts to the anhydride. This is illustrated in Fig. 2, showing the effect of oven treatment of samples 3 and 4 in Table 1. The polymer is stable at 50°C and below, but slow weight loss was observed even at 70°C, shown in Fig. 3. Reversion to the anhydride was confirmed by IR measurement on solid polymer samples treated at 90°C for 3 days. A continuous decrease of the acid and ester resonances at 1705 and 1730  $\text{cm}^{-1}$  and a simultaneous increase of the anhydride resonances at 1780 and 1850  $\text{cm}^{-1}$  were detected. The most rapid changes occurred during the first day of oven treatment.



**Isobam-6 Propyl Half Ester in n-Propanol**

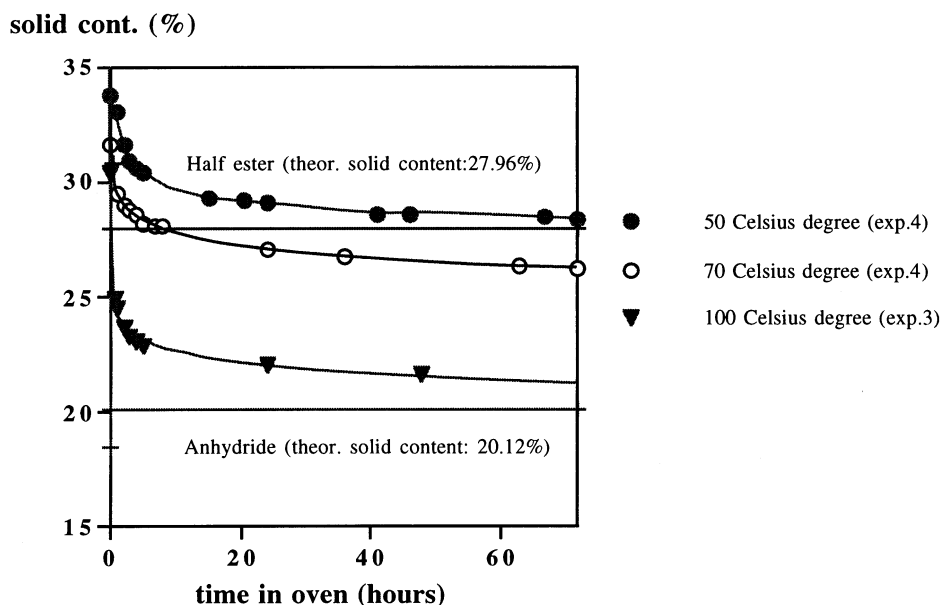


Figure 2. Isobam-6 propyl half ester in n-Propanol solid content (%).

Similar thermal behavior was observed with the butyl half ester of Isobam-6, the butyl and pentyl half esters of EMA and the butyl and hexyl half esters of Gantrez<sup>®</sup> AN 119, with small differences in the rates of reversion. (Gantrez<sup>®</sup> AN 119 is supplied commercially by ISP). The slowest was the reversion of the butyl half ester of EMA, and the fastest was that of the propyl half ester of Isobam-6.

A good linear correlation between the density of the polymer solution in 1-propanol and the polymer concentration (expressed in weight percentage) allows one to obtain the polymer concentration within a few minutes, shown in Fig. 4. In comparison, drying the samples to constant weight in the vacuum oven takes about two weeks. Density of the solutions was determined using a calibrated Gardner cup of known volume. A Mettler-Paar DMA-45 density meter has also been qualified for this method.

Acid content, or acid value of the polymers, expressed in units of meq/g (millimole acid per unit weight (g) of dry polymer) in Table 1 was determined by titration with sodium hydroxide. The polymer solution was diluted with 1-propanol to approximately 2% by weight, and the solution was titrated with 0.1 N sodium hydroxide solution. A more concentrated solution of polymer or base caused the polymer to precipitate and/or partially hydrolyze to the diacid, which leads to erroneous results. The theoretical acid content of the propyl and butyl half ester of the IB/MAn copolymer are 4.67 and

**Isobam-6 Propyl Half Ester in n-Propanol**

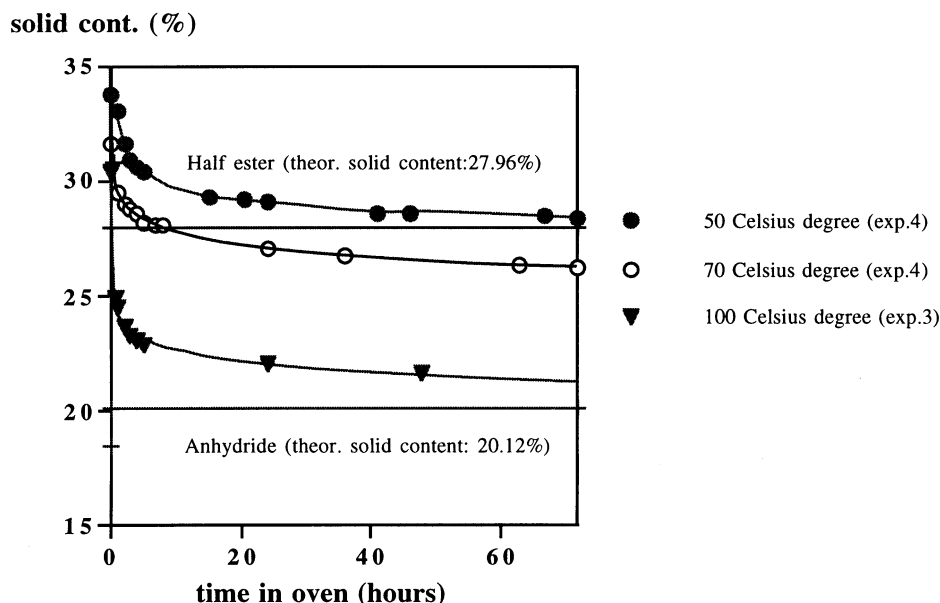


Figure 3. Isobam-6 Propyl half ester in n-Propanol solid content (%).

4.38 meq/g, respectively, which is in good agreement with the acid values listed in Table 1.

The glass transition temperature ( $T_g$ ) of the propyl half-ester of Iso-bam-10 polymer was determined to be 65–68°C, using a TA Instruments 2920 Differential Scanning Calorimeter. The inflection point in the reversible heat flow curve on the second heat was recorded as the  $T_g$ , samples were heated from –20°C to 95°C at 4°C/min. It is necessary to keep the scanning temperature below 100°C when analyzing the half-ester polymers to avoid reversion of the ester to anhydride, which would give an erroneously high  $T_g$  value. Thin, coated films of the polymer, as expected in accordance with the glass transition temperature, are resistant to cracking and curl under standard testing conditions.

Molecular weight of selected polymer samples was determined by size exclusion chromatography, shown in Table 2. A Waters 150C instrument equipped with 2 PL Gel mixed bed columns and an external RI detector was used with THF eluent at 1 ml/min, and calibrated with polystyrene standards. The increase in molecular weight as compared to that of the anhydride copolymer IB/MAn, also shown in Table 2, corresponds to the ester content of the copolymer. It is slightly lower than expected, based on the acid and solid content measurements and the disappearance of the anhydride



### Solid Content versus Density of the Propyl Half Ester of Isobam in n-Propanol

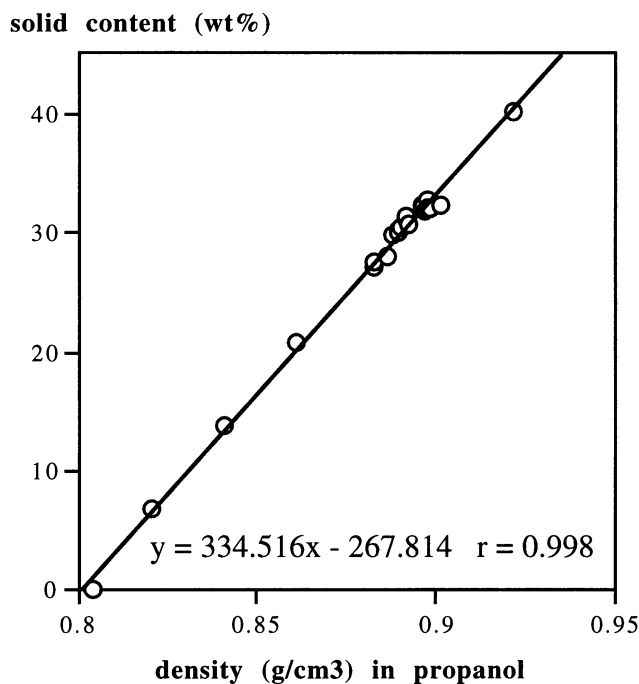


Figure 4. Solid content vs. density of the Propyl half ester of Isobam in n-Propanol.

resonances in the IR spectrum. This may be ascribed to differences between the methods of the molecular weight measurement.

Viscosity of the polymer solutions, listed in Table 1, was measured with a Brookfield viscometer at room temperature (22°C). Selected polymer solutions were also blended with poly(vinyl butyral), commercially available

Table 2. Molecular Weight of IBMA and Its Alkyl Half Esters

Sample	Ester	Anhydride (Grade)	M <sub>n</sub>	M <sub>w</sub>	PDI (M <sub>w</sub> /M <sub>n</sub> )	M <sub>w</sub> * (Initial)
1	butyl	Isobam-6	49,400	112,000	2.27	80,000
4	propyl	Isobam-6	41,400	99,900	2.41	80,000
12	propyl	Isobam-4	31,000	75,000	2.42	55,000
16	propyl	Isobam-10	77,200	197,100	2.55	160,000

\* Weight average molecular weight of the anhydride copolymer (Isobam), reported by the supplier, Kuraray Co.



**Table 3.** Rheology of the Blends of Propyl Half Ester of IBMA with Butvar

Polymer	Butvar content of Blend (wt%)	Viscosity (cPs) (@1 sec <sup>-1</sup> )	Viscosity (cPs) (@10,000 sec <sup>-1</sup> )
Propyl half ester of Isobam-6	14.3	3,400	215
Propyl half ester of Isobam-6	20.0	6,500	258
Propyl half ester of Isobam-10	14.3	15,400	424

under the trade name Butvar<sup>®</sup> (grade B72). Shear thinning behavior of these blends was confirmed by viscosity measurements at high and low shear rates using a Bohlin VOR rheometer with tapered plug geometry. Results are summarized in Table 3 for low (1 sec<sup>-1</sup>) and high shear rates (10,000 sec<sup>-1</sup>). The solutions are all shear thinning, but it is more pronounced in the blend with higher poly(vinyl butyral) content, and with the polymer of higher molecular weight. Shear thinning is attributed to H-bonding interactions of the polymers, which break down at higher shear rates.

### CONCLUSION

The propyl half ester of the alternating copolymer of isobutylene with maleic anhydride can be readily obtained as a solution in propanol by esterification of the dispersed polymer with the solvent. At elevated temperature (120°C) and pressure (about 25 psi) the reaction is complete in about 6.5 hours. The acid content of the polymer is close to the theoretical acid content of the half ester, 4.67 millimole acid/gram polymer. Thin, coated films of the polymer are resistant to cracking and curl. The polymer is thermally stable to at least 50°C. On prolonged heating of the dry polymer at higher temperatures, the ester group reverts to the anhydride. Density measurement of the polymer solution can be used as a rapid method to determine polymer concentration. Solutions of the polymer with poly(vinyl butyral) in 1-propanol are shear thinning. Shear thinning behavior is more pronounced with increasing molecular weight of the polymer and with higher poly(vinyl butyral) content, which is an advantage in high speed coating operations.

These polymers may be of practical use in various applications where high acid content combined with shear thinning in solution form and flexibility in a coated film form are desirable.

### ACKNOWLEDGMENTS

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