

reasonable reactivity in polymerization/copolymerization reactions.

This report summarizes our initial investigation of these possibilities.

Experimental

All chemicals and reagents used in this study were reagent grade and were used as received. All $^1\text{H-NMR}$ spectra were recorded at 300 MHz using a Varian Gemini 300 FT NMR on 10% wt/v solutions of polymer in d_6 -DMSO at ambient temperatures. All IR spectra were recorded on KBr pellets of polymer using a Nicolet 5DXB FTIR spectrometer. Molecular weight measurements were made using a GPC equipped with a Waters 510 pump, six Polymer Labs columns and a Waters 410 R.I. detector. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve. The solvent resistance of the polymer films was measured using 2-butanone and an Atlas AATCC Crockmeter. Impact resistance was measured with a Gardner Impact Tester employing a 4 lb. weight. Pencil hardness was measured with Berol pencils.

Monomer Synthesis

The monomer was synthesized from pugelone via a Wittig reaction as previously described (10). The monomer was purified by distillation from CaH_2 . B.p. = 87-89°/35 mm. Yield = 63%.

Polymerizations

The synthesis of a homopolymer of 3-methylene-p-menth-4(8)-ene (MME) using free radical initiation was attempted by weighing monomer (2.0 g) into a clean, dry screw cap vial followed by 1.5 wt% benzoyl peroxide. The monomer-initiator mixture was sparged with dry nitrogen and the vial was tightly sealed with a teflon lined screw cap. The vial was then placed in a bath maintained at 130°C. After 6.5 hr the vial was removed from the bath, cooled to ambient temperature, and 5 ml of cold methanol was added. No methanol insoluble polymer was observed. Analysis of the reaction mixture showed mostly unreacted monomer and small amounts of dimer and trimer. Because the failure to form polymer at 130°C could be due to a ceiling temperature effect, an experiment using the same levels of monomer and initiator was conducted at 75°C. After 7.0 hours no methanol insoluble polymer was obtained and almost the entire monomer charge was recovered unchanged.

Copolymerizations

Copolymers were synthesized by weighing 8.0g of MME into a 50 ml round bottom flask equipped with a reflux condenser, magnetic stirrer and nitrogen inlet. Maleic anhydride (MAH) (5.30g) or itaconic anhydride (ITAH) (6.05g) were then added followed by 2.0 wt % benzoyl peroxide and 10 ml of dry 2-butanone. The flask was immersed in a bath maintained at 75°C and the reaction was allowed to proceed,

under nitrogen, for 5.0 hours. The flask was then removed from the bath and the contents were allowed to cool to ambient temperature. The flask contents were added, with stirring, to an 8-fold excess of diethyl ether/petroleum ether (5/1, v/v). The precipitated copolymers were isolated by filtration and were purified by reprecipitation from chloroform solution into diethyl ether/petroleum ether. The polymers were dried in vacuo at 35°C for 72 hours, then weighed to determine conversion.

Coatings Formulation

Coatings were formulated by combining 2.0 grams of polymer with 1.4g of diepoxide (Araldite CT 6060, Epoxy equivalent weight = 187) for the itaconic anhydride copolymer and 2.0 grams of polymer with 1.5g of diepoxide for the maleic anhydride copolymer. In both cases 0.09g of a cure catalyst (aluminum acetylacetonate) was added, followed by sufficient 2-butanone to result in a solution that was 50 wt % solids. Drawdowns were made over aluminum panels with a #34 wire wound drawdown bar which yields a dry film thickness of 1.2-1.4 mil. The panels were then baked in a forced air oven at 150°C for 0.5 hours.

Results and Discussion

Table 1 lists the results of the polymerization experiments.

TABLE 1

Polymerization Results

Polymer	M ₁	M ₂	M ₁ of M ₁ in Feed	PZN Temp. (°C)	PZN Time (h)	Conv. %	M _n	M _w
PUG1	MME	-	1.0	130	6.5	0	-	-
PUG2	MME	-	1.0	75	7.0	0	-	-
PUG3	MME	MAH	0.5	75	5.0	3.0	2000	2700
PUG4	MME	ITAH	0.5	75	5.0	12.0	1700	2200

The attempted free radical initiated homopolymerization of MME was not successful. The MME radical may be too unreactive to add to MME monomer, the MME radical may not form under the conditions used or a ceiling temperature effect may be operating even at 75°C. Answering these questions requires a more detailed investigation, which is currently underway.

The copolymerization of MME with MAH or ITAH did not yield high conversions or high molecular weights, but was possible. Co-

polymer composition was determined by $^1\text{H-NMR}$ and IR spectroscopy (Figures 1 and 2). The signals are assigned as shown in the Figures (11,12). The PUG3 copolymer was 50 mol % MAH, while PUG4 was 53 mol % ITAH. Based on these compositions coating formulations were prepared and films made over aluminum as previously described (3). Table 2 lists the properties evaluated and the results obtained for each of the films.

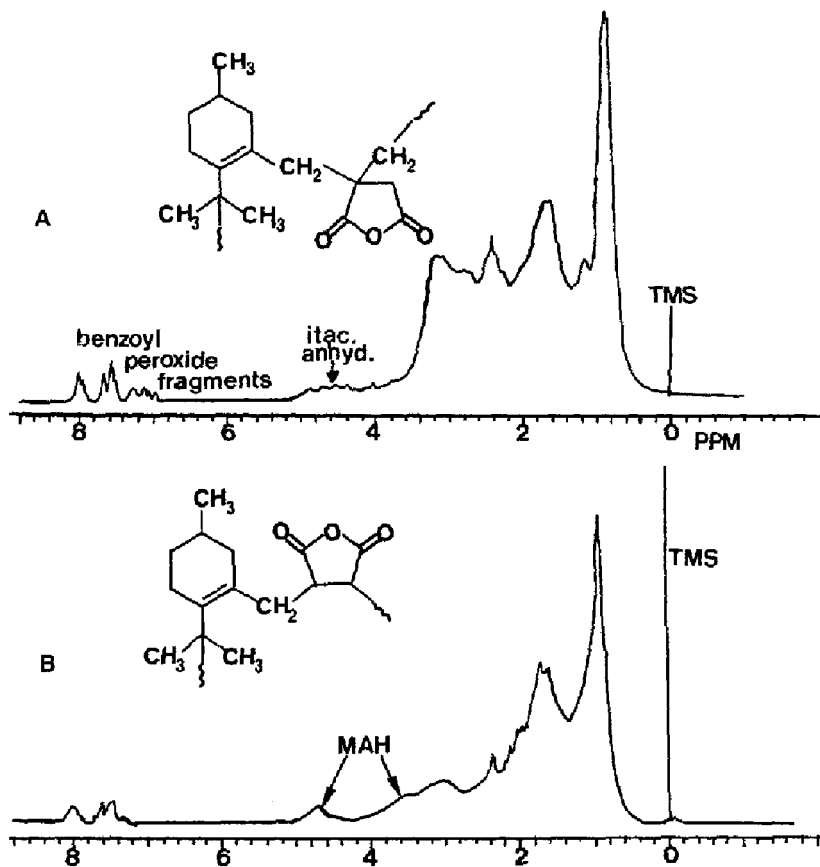
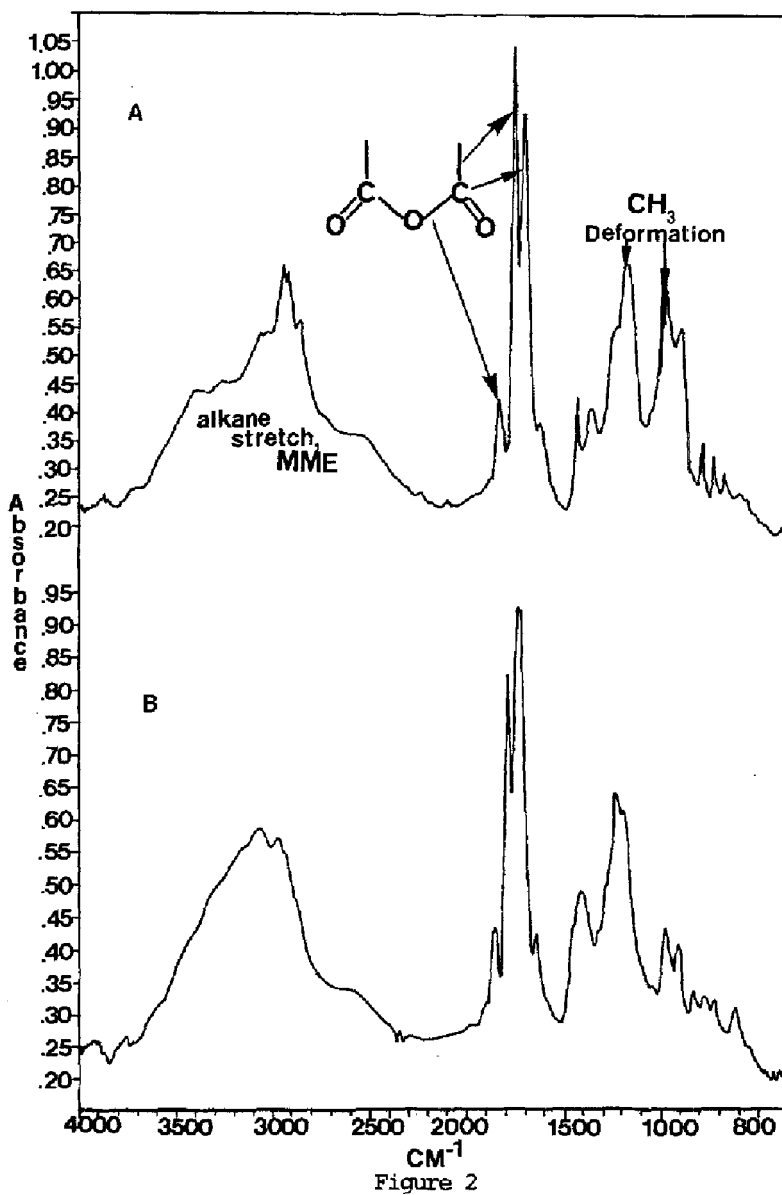


Figure 1

$^1\text{H-NMR}$ spectra of: A) Itaconic anhydride-MME copolymer;
B) Maleic anhydride-MME copolymer



IR Spectra of: A) Maleic anhydride-MME copolymer
Itaconic anhydride-MME copolymer

TABLE 2

Film Properties

Polymer	2-Butanone Double Rubs	Forward Impact Resistance, in lbs.	Reverse Impact Resistance, in lbs.	Pencil Hardness
PUG3	100	20	20	2H
PUG4	400+	10	5	3H

For PUG3 the number of double rubs reported is the number required to break through the film to the bare metal. For PUG4 the test was stopped after 400 rubs because there was no observable effect on the film. For PUG3 the breakthrough to bare metal occurred after only 100 rubs, the reason(s) for such a wide difference between PUG3 and PUG4 may be that the anhydride moiety of itaconic anhydride in the copolymer is more available for reaction than the MAH of PUG3, PUG4 contains slightly more anhydride units than PUG3 and because of lower molecular weight PUG4 has a higher crosslink density. These factors individually would not be expected to yield such a large difference but together, along with some as yet undefined factors, could account for the difference in solvent resistance. In any case, the films made from the MME and the diepoxide perform much better than films made from MME or diepoxide alone. Such films, even after baking in the presence of the aluminum acetylacetonate, withstand only 2-6 2-butanone double rubs before breaking through to bare metal.

The other film properties are typical of those obtained for thermoset polymers with relatively high crosslink densities (14). The films are hard and brittle with the PUG4 film being harder and more brittle, reflecting the higher crosslink density of this film.

Conclusions

The title monomer, 3-methylene-p-menth-4(8)-ene, was synthesized in good yield from pugelone. Homopolymerization of the monomer via free radical initiation was unsuccessful at the temperatures employed. Possibly, a ceiling temperature effect may be responsible for this lack of polymerizability but more work will have to be done to determine if this is so. It was possible to produce low molecular weight copolymers of MME with MAH or ITAH in low yield. Films of these copolymers cured with a diepoxide proved to have good to outstanding solvent resistance and hardness but were brittle.

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