

**Table I. Reaction Parameters and Results for Manganese Dioxide Catalyzed Hydration of Nitriles to Amides**

Nitrile	Concn	Temp, °C	Conversion, <sup>a</sup> %	Contact time, hr	
				Obsd	Extrapolated <sup>b</sup>
Acetonitrile	1M	70	63	1.45	2.3
Propionitrile	1M	70	73	2.25	3.1
<i>n</i> -Butyronitrile	0.5M	70	83	3.00	3.6
<i>n</i> -Butyronitrile <sup>c</sup>	1M	70	67	2.75	4.1
Isobutyronitrile	0.5M	75	71	2.75	3.9
Succinonitrile	0.5M	100	100	0.50	0.5
Adiponitrile	0.5M	100	59	0.75	1.3
Acrylonitrile <sup>d</sup>	1M	70	65	2.83	4.4
Benzonitrile <sup>e</sup>	1M	85	20	0.41	2.1
3-Cyanopyridine <sup>e</sup>	1M	85	100	0.51	0.5
Acetone cyanohydrin	1M	25	60	2.67	4.5

<sup>a</sup> Yields for the compounds in this table are essentially quantitative. <sup>b</sup> Contact times are extrapolated to 100% conversion. <sup>c</sup> Aqueous feed solution was emulsified with the aid of 0.04% Triton X-200. <sup>d</sup> A polymerization inhibitor was added to the feed solution. <sup>e</sup> In a catalyst exhaustion study there was no significant loss in catalyst activity after more than 60 grams of product/gram of catalyst had been formed.

temperatures above about 50°C are generally necessary for practical purposes. At atmospheric pressure the boiling point of the nitrile-water mixture imposes the upper temperature limit. The reaction may be conducted under pressure to increase reaction temperature and therefore rate, but the additional difficulty does not seem to warrant such operation.

The reaction time (contact time) will vary somewhat depending upon the reactivity of the nitrile. As indicated in Table I, typical contact times fall in the range of less than one to a few hours. In general, the order of reactivity is approximately cyanopyridines > aromatic nitriles > aliphatic nitriles > vinyl cyanides. Various electronic and steric factors, although they have not been thoroughly investigated, undoubtedly come into play.

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## Preparation and Wetting Characteristics of Some Poly(Fluorinated Aromatic Glycidyl Ethers)

Some fluorine-substituted aromatic glycidyl ethers were homopolymerized by means of a triethylaluminum-water catalyst. Films of these polymers cast from *m*-xylenehexafluoride solution were clear and approached Teflon in their low critical surface tensions of wetting. The desirable wettability characteristics, however, were obtained with a modest amount of fluorine substitution.

There has been much interest in recent years in the polymerization of epoxides by organometallic catalysts. Vandenberg (1969) has made an extensive study of the syntheses, stereochemistry, structure, and polymerization mechanisms. Price and Brecker (1969), Ueshima et al. (1966), and Kuntz and Kroll (1970) have likewise contributed substantially to the area. A catalyst system of triethylaluminum and water (TEA-H<sub>2</sub>O) has proved to be particularly potent for high-molecular-

weight polymerizations which often yield stereoregular polymers of the polyether type.

Pittman et al. (1970) have recently prepared some fluoro-epoxy polymers by use of Lewis acid catalysts and studied the wetting characteristics of films of these materials. In addition, Pittman et al. (1968) and Elmer et al. (1968) have described some fluorinated aliphatic glycidyl ethers in the patent literature.

**Table I. Polymerization Parameters and Physical Properties of Representative Fluorinated Aromatic Epoxies**

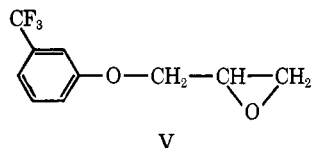
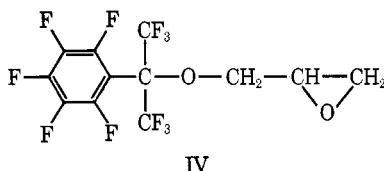
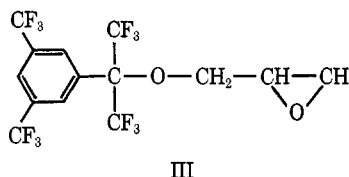
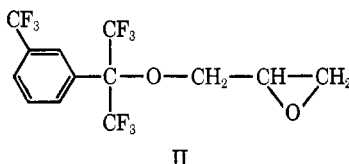
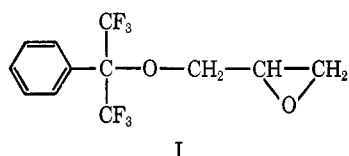
Material	Reaction medium	Relative rate of reaction <sup>a</sup>	Initial product	$\eta_{inh}$ at 38°C <sup>b,c,d</sup>	$\Delta\eta_{inh}/\Delta C$	Concn used for films <sup>b</sup>	$\theta_{H_2O}$ at 22°C, °C	$\gamma_c$ (dyn/cm) at 22°C
I <sup>e</sup>	Ether	Rapid	Ether-insol, rubbery gel	1.44	...	1.00	101	20.2
II-a/	Ether	Slow	Ether-sol, clear gel	0.80 (0.26)	...	0.26	104	19.4
II-b	XHF	Rapid	Tough insol rubber	3.86	-2.97	0.48	102	21.5
III-a	Ether-XHF	Slow	Sol, yellowish gel	0.97 (1.40)	...	1.40	104	19.2
III-b	Ether	Rapid	Tacky insol gel	2.04	-0.68	0.68	105	19.1
IV	XHF	Rapid	Thick insol gel	2.78	-1.23	0.59	102	20.2
V	Ether	Very rapid	Tacky insol gel	1.32	-4.09	1.35	103	18.5

<sup>a</sup> "Rapid" would describe the case in which considerable thickening has occurred within 5-10 min, whereas a "slow" reaction would take an hour or more before thickening is noticeable. <sup>b</sup>  $\eta_{inh}$  in units of reciprocal concn. <sup>c</sup> Concn in units of gram polymer/100 cc XHF. <sup>d</sup> Concn is understood to be 0.50 g/100 cc XHF unless otherwise noted in parentheses. <sup>e</sup> Unreacted monomer was extracted with *n*-heptane in place of pptn by  $C_6H_{12}$ . <sup>f</sup> Characterization was of the toluene-insol fraction (46 wt %) of the polymer.

Previous work from this laboratory (Reines et al., 1970, 1971; O'Rear et al., 1971) described the syntheses of a number of glycidyl ethers derived from substituted 2-phenyl-2-hexafluoropropanol and from similar disubstituted intermediates. The most highly fluorinated of these have now been homopolymerized with TEA-H<sub>2</sub>O catalyst systems to produce linear polymers of limited solubility in 1,3-di(trifluoromethyl)benzene, commonly known as *m*-xylenehexafluoride (XHF). Our intent is to describe some of these polymerizations and the wetting characteristics of films of the resultant polymers.

#### Experimental

**Monomers.** Five materials of analytical quality (carbon, hydrogen, and fluorine analysis within  $\pm 0.3\%$  of theoretical) were available from our previous work.



All these glycidyl ethers are liquid at room temperature and were fractionated by precision distillation. (The homopolymers derived from the monomers above will be referred to below as P-I, P-II, etc.)

**Catalyst.** A catalyst of TEA-H<sub>2</sub>O in 1-0.6 mole ratio in ether solution was prepared and used according to Vandenberg (1969). Two batches were used with equal success. The batch #1 was made to his specifications except that it was prepared from a 10% solution of TEA in heptane (available from Ethyl Corp.) instead of from a 25% solution. Batch #2 was considerably more dilute (70% ether by volume), so that no further dilution of the contents of the reaction flask was necessary when polymerization was initiated.

#### Results

Table I summarizes the polymerization reactions and some physical properties of representative polymers. All polymerizations were run for about 18 hr. In nearly all instances, the product removed from the reaction flask was a tacky gel. The "work-up" of the polymers generally consisted in dissolving the gel in XHF, washing to neutrality in a separatory funnel with dilute HCl and distilled water, and drying over anhydrous sodium sulfate. Next, the polymer was precipitated from solution with reagent-grade cyclohexane, air-dried under cover, and finally redissolved in XHF. The final solutions proved to be monomer-free by chromatographic analysis on a Beckman GC-2A.

Inherent viscosities,  $\eta_{inh}$ , were run in a Cannon-Ubbelohde dilution microviscometer at  $38.0 \pm 0.1^\circ\text{C}$ .

Thin films for wettability studies were cast by spreading smooth layers of the polymer solutions over acid-cleaned glass slides with disposable Pasteur pipettes. The slides were allowed to dry in the air for an hour before being placed in a clean asbestos oven for 2 hr at  $110^\circ\text{C}$ . The work was carried out in an air-conditioned, dust-free laboratory. The films were all clean and quite smooth, even under  $500\times$  magnification. They were slightly rigid and adhered tenaciously to the glass slides.

The wettability studies are reported in terms of the contact angle,  $\theta_{H_2O}$ , made by triply distilled water on these films, and their critical surface tensions of wetting,  $\gamma_c$ , determined with a series of five *n*-alkanes. Each of the alkanes was purified of polar contaminants before use by percolation through a column of alumina and Florisil into dark bottles and was kept refrigerated when not being used. Contact angles were measured at ambient ( $22.0 \pm 0.5^\circ\text{C}$  and 40-50% RH) on an NRL contact-angle goniometer (Fox and Zisman, 1950). The cosines of the contact angles of the *n*-alkanes were

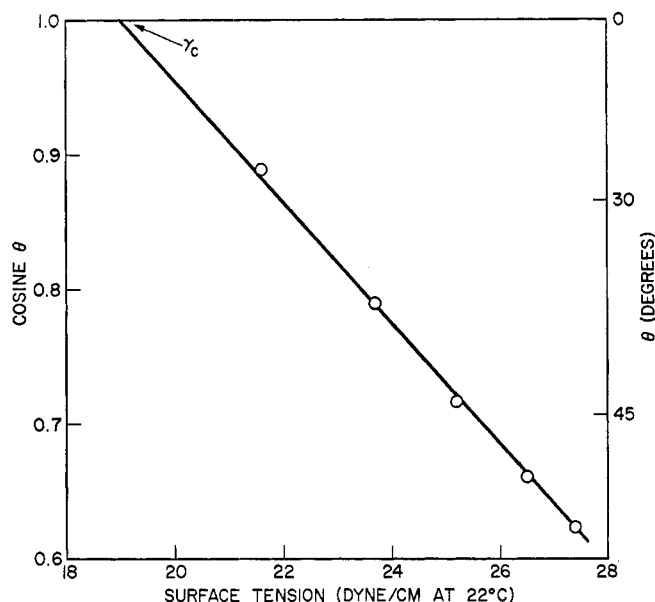


Figure 1. Typical Zisman-type plot of cosine  $\theta$  vs. surface tension for *n*-alkanes on epoxy film. Epoxy is P-III-b

plotted against the surface tensions,  $\gamma_{LV}$ , of these liquids, and the intercept of the resultant straight line at  $\cos \theta = 1$  ( $\theta = 0^\circ$ ) is denoted as  $\gamma_c$ , an inherent property of the solid surface itself (Fox and Zisman, 1950). An example of one such Zisman-type plot is shown in Figure 1.

#### Discussion

The main focus of our investigation was on the aromatic-containing poly(fluorinated glycidyl ethers), as the presence of the aromatic group promised enhanced toughness and stability. In their hydro- and oleophobicity, all the fluorinated aromatic epoxies approach Teflon (polytetrafluoroethylene), for which  $\theta_{H_2O} \approx 102^\circ$  and  $\gamma_c = 18.5$  dyn/cm.

It was initially surprising to discover little difference in wettability among P-I-P-IV. This might be because the outer surface of the polymer chains consisted mainly of perfluoromethyl groups protruding from the hexafluoroisopropyl moiety of the monomer unit. Molecular models seem to confirm the hypothesis that the pendant groups along the polymer backbones are quite densely packed and that a preferred arrangement in the side chains might exist when the phenyl groups are tucked beneath the bulky hexafluoroisopropyl moiety. P-V, which lacked the hexafluoroisopropyl moiety, was similar in nearly all aspects to P-I-P-IV, particularly in wettability. One difference with P-V was that the alkane drops on its surface tended to "swell" (i.e., gave inordinately high-contact angles) before coming to an equilibrium contact angle, as though some soluble nonsurface active species were being leached out of the film.

Poly(phenyl glycidyl ether) (PPGE) would seem to be a good reference material against which to compare the fluorinated analogs with regard to wettability. Unfortunately, not enough TEA-H<sub>2</sub>O-catalyzed PPGE would dissolve in any of a variety of solvents to allow us to cast a film. According to Vandenberg (1969), the PPGE thus produced is an isotactic, high-molecular-weight polymer, whereas our fluorinated aromatic epoxies are amorphous. Attempts to obtain a soluble PPGE by polymerizing the monomer with potassium tert-butoxide in dimethyl sulfoxide according to Price et al. (1969) were unsuccessful.

#### Conclusions

The fluorinated aromatic epoxies synthesized in our laboratory show promise for applications which require durable, tenaciously adhesive films with good hydro- and oleophobic characteristics. This study, however, seems to indicate that only a modest amount of fluorine substitution (e.g., as in P-I or P-V) is needed to obtain near optimal hydro- and oleophobicity.

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