

## Preparation and Copolymerization of *p*-Vinylphenylalkylcarbinol

It may be of interest to examine the chemical reactions, copolymerizations, and polymer reactions of styrene derivatives having reactive hydroxy groups. However, there are very few reports of such monomers and polymers have appeared in the literature. It was previously reported that *p*-vinyl-benzylmethylcarbinol<sup>1</sup> (*p*-VBMC) and *p*-vinyl-benzylethylcarbinol<sup>2</sup> (*p*-VBEC) react with phenyl isocyanate to yield urethane compounds which gave homopolymers soluble in ethanol, tetrahydrofuran, and dioxane and insoluble in toluene, petroleum ether, and carbon tetrachloride. And it was found that the both monomers could be well copolymerized with acrylonitrile (AN). This work was carried out to study some characteristics of the polymerizations of *p*-vinylphenyldimethylcarbinol (*p*-VPhDMC), *p*-vinylphenylmethylethylcarbinol (*p*-VPhMEC), and *p*-vinylphenyldiethylcarbinol (*p*-VPhDEC).

### EXPERIMENTAL

#### Monomers

*p*-VPhDMC was prepared by the same method described in the literature.<sup>3</sup> The clear white crystal after several recrystallizations had a melting point of 42.9°C. The NMR spectra showed for *p*-VPhDMC: phenyl H,  $\tau$  2.76;  $-\text{CH}=\text{CH}_2$ ,  $\tau$  3.14–4.96;  $-\text{OH}$ ,  $\tau$  7.68;  $-\text{CH}_3$ ,  $\tau$  8.52. *p*-VPhMEC was prepared by hydrolysis after the reaction of *p*-vinylphenylmagnesium chloride and methyl ethyl ketone in THF at 60°C. The appearance of this monomer obtained by several vacuum distillations was a transparent, viscous liquid having bp 90.5–91.5°C/2.2 mm Hg,  $n_D^{20}$  1.5494.

ANAL. Calcd: C, 81.77%; H, 9.15%. Found: C, 81.43%; H, 9.02%.

TABLE I  
Infrared Spectra of Monomers

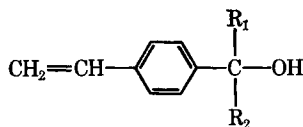
<i>p</i> -VPhDMC		<i>p</i> -VPhMEC		<i>p</i> -VPhDEC	
Assignment	Ab-sorp-tion band, $\mu$	Assignment	Ab-sorp-tion band, $\mu$	Assignment	Ab-sorp-tion band, $\mu$
$\nu_{\text{OH}}$	3.00	$\nu_{\text{OH}}$	2.92	$\nu_{\text{OH}}$	2.89
$\nu_{\text{C}=\text{C}}$	6.12	$\nu_{\text{C}=\text{C}}$	6.13	$\nu_{\text{C}=\text{C}}$	6.13
$\delta_{\text{C}-\text{H}}$ ( $-\text{CH}=\text{CH}_2$ )	10.06	$\delta_{\text{C}-\text{H}}$ ( $-\text{CH}=\text{CH}_2$ )	10.10	$\delta_{\text{C}-\text{H}}$ ( $-\text{CH}=\text{CH}_2$ )	10.10
$\delta_{\text{C}-\text{H}}$ ( $-\text{CH}=\text{CH}_2$ )	11.00	$\delta_{\text{C}-\text{H}}$ ( $-\text{CH}=\text{CH}_2$ )	11.00	$\delta_{\text{C}-\text{H}}$ ( $-\text{CH}=\text{CH}_2$ )	11.07
$\delta_{\text{C}-\text{H}}$ ( <i>p</i> -substd.)	11.82	$\delta_{\text{C}-\text{H}}$ ( <i>p</i> -substd.)	11.88	$\delta_{\text{C}-\text{H}}$ ( <i>p</i> -substd.)	11.90

The NMR spectra showed for *p*-VPhMEC: phenyl H,  $\tau$  2.79;  $-\text{CH}=\text{CH}_2$ ,  $\tau$  3.15–4.96;  $-\text{OH}$ ,  $\tau$  6.97;  $-\text{CH}_2-\text{CH}_3$ ,  $\tau$  8.10–8.48;  $-\text{CH}_3$ ,  $\tau$  8.58;  $-\text{CH}_2-\text{CH}_3$ ,  $\tau$  9.16–9.40. *p*-VPhDEC was prepared by the same method as above described, except that diethyl ketone was used in place of methyl ethyl ketone.

ANAL. Calcd: C, 82.06%; H, 9.54%. Found: C, 82.26%; H, 9.72%.

The product was a clear, viscous liquid, bp 93.5–94.0°C/2.0 mm Hg and  $n_D^{20}$  1.5432. The NMR spectra showed for *p*-VPhDEC: phenyl H,  $\tau$  2.75;  $-\text{CH}=\text{CH}_2$ ,  $\tau$  3.23–4.92;  $-\text{OH}$ ,  $\tau$  7.63;  $-\text{CH}_2-\text{CH}_3$ ,  $\tau$  8.22–8.35;  $-\text{CH}_2-\text{CH}_3$ ,  $\tau$  9.20–9.35. *p*-Chlorostyrene (*p*-ClSt) was prepared by the Walling method:<sup>4</sup> It had bp 62.0–62.5°C/6.0

mm Hg and  $n_D^{20}$  1.5646. Styrene ( $n_D^{20}$  1.5468) was purified by vacuum distillation after washing with 10% KOH solution and water and drying over anhydrous calcium chloride.



- I;  $\text{R}_1, \text{R}_2 = -\text{CH}_3$   
 II;  $\text{R}_1 = -\text{CH}_3, \text{R}_2 = -\text{C}_2\text{H}_5$   
 III;  $\text{R}_1, \text{R}_2 = -\text{C}_2\text{H}_5$

AN ( $n_D^{20}$  1.3912) was used after several vacuum distillations. Infrared spectra for *p*-VPhDMC, *p*-VPhMEC, and *p*-VPhDEC are summarized in Table I.

### Solvent

Dioxane was dried with solid KOH and metal sodium after washing with concentrated HCl and was purified by distillation (bp 100.5–100.6°C,  $n_D^{20}$  1.4223) after treatment with  $\text{Al}_2\text{O}_3$ . THF was purified by distillation after the dehydration with metallic sodium; bp 65.5–66.0°C,  $n_D^{20}$  1.4065. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol.

### Polymerization

All polymerizations and copolymerizations were carried out in 50 wt-% dioxane at 60°C under nitrogen in a sealed tube with addition of 0.2 wt-% AIBN for 1–5 hr. Polymers were purified by the reprecipitation method by using THF as solvent and petroleum ether as nonsolvent. In the case of copolymerization, before the polymerization conversion reached 10%, polymerization mixture was poured into petroleum ether; and precipitation was repeated several times. The polymers were then dried under reduced pressure to reach to constant weight at room temperature.

## RESULTS AND DISCUSSION

It has been pointed out that secondary alcohols such as *p*-VBMC and *p*-VBEC give the urethane compounds on reaction with phenyl isocyanate at room temperature without any catalyst. However, no change occurred when the mixture of *p*-VPhDMC and phenyl isocyanate allowed to stand at room temperature for 24 hr. On warming the mixture at 40°C for 1.5 hr on a water bath, white crystals precipitated, which on recrystallization yielded white needles, mp 236°C. The white crystals were identified as 1,1-diphenylurea by means of elemental analysis and infrared spectroscopy. In this reaction we did not investigate further, but it was presumed that 1,1-diphenylurea and *p*-vinyl- $\alpha$ -methylstyrene were produced by dehydration.

Conversions of *p*-VPhDMC, *p*-VPhMEC, and *p*-VPhDEC were 32.9, 20.6, and 25.0%, respectively, for 5 hr homopolymerization. All the polymerization products were white powders, soluble in methanol, THF, and dioxane but insoluble in benzene, petroleum ether, and carbon tetrachloride. When the polymers were dissolved in THF and spread on glass plates and THF was removed by heating in an oven at 60°C for 5 hr, hard, clear films were formed. NMR spectra showed for poly(*p*-VPhDMC): phenyl H,  $\tau$  2.75–3.42;  $-\text{OH}$ ,  $\tau$  6.30;  $-\text{CH}-\text{CH}_2$ ,  $\tau$  7.20;  $-\text{CH}-\text{CH}_3$ ,  $\tau$  8.20;  $-\text{CH}_3$ ,  $\tau$  8.48; and for poly(*p*-VPhMEC): phenyl H,  $\tau$  2.80–3.46;  $-\text{OH}$ ,  $\tau$  6.22;  $-\text{CH}-\text{CH}_2$ ,  $\tau$  7.20;  $-\text{CH}-\text{CH}_3$ ,  $-\text{CH}_2-\text{CH}_3$ ,  $\tau$  8.30;  $-\text{CH}_3$ ,  $\tau$  8.53;  $-\text{CH}_2-\text{CH}_3$ ,  $\tau$  9.14–9.20.  $(\text{CD}_3)_2\text{CO}$  was used as the solvent for NMR spectral measurements. The absorptions in the infrared spectra which indicate  $\nu_{\text{C}=\text{C}}$  disappeared after polymerization of the all monomers. It is apparent that the monomers were polymerized by a radical mechanism. The monomer reactivity ratios of *p*-VPhDMC( $M_1$ ), *p*-VPhMEC( $M_2$ ), and *p*-

VPhDEC( $M_2$ ) were calculated by graphically solving the Fineman-Ross equation,<sup>5</sup> and  $Q$  and  $e$  values were estimated by the Alfrey-Price equation.<sup>6</sup>  $r_1$ ,  $r_2$ ,  $Q$ , and  $e$  values are shown in Table II.

TABLE II  
 $r_1$ ,  $r_2$ ,  $Q$ , and  $e$  values

	$r_1$	$r_2$	$r_1r_2$	$e$	$Q$
AN- <i>p</i> -VPhDMC	0.05	0.41	0.02	-0.8	0.80
AN- <i>p</i> -VPhMEC	0.06	0.39	0.02	-0.8	0.67
AN- <i>p</i> -VPhDEC	0.04	0.38	0.02	-0.8	0.97
<i>p</i> -ClSt- <i>p</i> -VPhDMC	1.24	0.53	0.66	-0.9	0.85
<i>p</i> -ClSt- <i>p</i> -VPhMEC	1.43	0.33	0.47	-1.2	0.97
St- <i>p</i> -VPhMEC	0.79	1.25	0.99	-0.7	1.17

The three monomers have similar copolymerizabilities, with AN, despite the differences of the substituents, as can be seen in Table II. The  $e$  values indicate the substituents donate electrons to the vinyl groups.

#### References

1. K. Anda and S. Iwai, *Kogyo Kagaku Zasshi*, **70**, 557 (1967).
2. K. Anda and S. Iwai, unpublished results.
3. T. Kunitomo, S. Tanimoto, and R. Oda, *Kogyo Kagaku Zasshi*, **68**, 1967 (1965).
4. C. Walling and B. Woltstirn, *J. Amer. Chem. Soc.*, **69**, 852 (1947).
5. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
6. T. Alfrey and C. Price, *J. Polym. Sci.*, **2**, 101 (1947).

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