Copolymerization of 2-Methoxy-4-Vinylphenol with Fluorinated Acrylic Monomers: Water-Repellent Properties of Copolymer

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Synopsis

To prepare the copolymer, which is water and oil repellent and contains the hydroxyl group, 2-methoxy-4-vinylphenol (VG: M_1) is copolymerized with the fluorinated acrylic monomer (M_2). The copolymerizability of VG (vinyl guaiacol) with pentadecafluoroctylacrylate (PDFOA) is best ($r_1 = 0.217, r_2 = 0.0751$). The critical surface tension γ_C of the copolymer of $F_1 = 0.451$ (F_1 is the ratio of M_1 units in the copolymer) is estimated to be 13.5 dyne/cm which is close to that of the homopolymer ($F_1 = 0$). The γ_C of the other copolymers are so small that they are 18.5 dyne/cm for copoly(VG–trifluoroethylmethacrylate) of $F_1 = 0.491$ and 17.8 dyne/cm for copoly(VG–fluoropentylmethacrylate) of $F_1 = 0.392$. Thus, these copolymers are water and oil repellent. Further, because of the hydroxyl, they provide hydrogen bonding to hydroxyapatite of teeth.

INTRODUCTION

Vinyl guaiacol (VG) (2-methoxy-4-vinylphenol) is prepared from vaniline produced from lignin[1,2] and becomes a model compound for lignin by the dehydrogenation polymerization of VG.[3,4]

$$CH_2\!\!=\!\!CHG \qquad VG \ (G = \text{—}\underset{OCH_3}{\overset{}{\bigcirc}}\text{—OH})$$
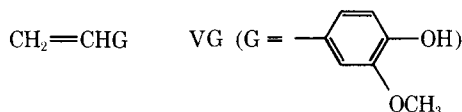
In radical polymerization, VG is considered to be an inhibitor, because of a hydroxy group, when the usual initiator 2,2′-azobisisobutyronitrile (AIBN) is used.[5,6] Thus, VG was polymerized by using tributylborane as an initiator.[6,7] However, *p*-vinylphenol (VP) copolymerizes with fluorinated acrylic monomers in the presence of AIBN,[8] in spite of VP possessing the hydroxyl group. The copolymer, water and oil repellent, provides hydrogen bonding to the hydroxyapatite of teeth, because of the fluorinated alkyl and hydroxyl groups. Thus, when VG copolymerizes with the fluorinated monomer, the copolymer obtained has properties similar to the copolymer containing fluorinated monomer and VP. VG was, therefore, copolymerized with some fluorinated monomers and the water and oil repellent properties of the copolymer were examined in terms of the critical surface tension.

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EXPERIMENTAL

VG was prepared by the previous method.[2] 2,2,2-Trifluoroethylmethacry-late (TFEM), 1H,1H,5H-octafluoropentylmethacrylate (OFPM), and 1H,1H-pentadecafluorooctylacrylate (PDFOA) were purchased from PCR Research Chemicals, Inc., and purified by following the previous methods.[8] AIBN used as initiator was recrystallized from methanol.

Monomer solutions containing [AIBN] = 0.0212 mol/liter were added to glass ampoules. VG and PDFOA did not dissolve in each other without added solvent; they dissolved in acetone. Thus, 50% acetone was also added to the ampoule for the VG–PDFOA system. The solutions were degassed by the freeze–thaw technique. The ampoule was then sealed under vacuum. The polymerization was conducted at $60 \pm 0.05°C$ in a water bath. The fluorinated monomer and the copolymer and VG were separated by adding petroleum ether to the solution: the fluorinated monomer would only dissolve in the petroleum ether. The polymer and VG were dissolved in acetone and the polymer was precipitated into water. Here, the copolymer, containing PDFOA units >50%, did not dissolve in acetone, but in 1,1,2-trifluoro-1,2,2-trichloroethane (FCE), and, therefore, was purified by using FCE and methanol. The purified polymer was dried in a vacuum.

The monomer composition in the copolymer was estimated by NMR. The intrinsic viscosity was measured in acetone or FCE at $30.0 \pm 0.05°C$. Poly-mer-coated microscope slides were prepared.[8] The contact angles of a series of alkanes and water were determined using an Erma G1-type microscope.

RESULTS AND DISCUSSION

Copolymerization

^{1}H NMR spectra of poly(VG), poly(PDFOA), and copoly(VG–PDFOA) are shown in Figure 1. In the NMR spectrum of poly(PDFOA), the absorptions at 1.1–2.25, 2.25–2.8, and 4.2–5.0 ppm are for $—CH_2—$ of the main chain, $—CH—$ of that, and $—OCH_2CF_2—$ of the side chain, respectively, because their area ratio is 2:1:2 and the absorption at 4.2–5.0 ppm is separated into three peaks by the neighboring two fluorines. In the NMR spectrum of poly(VG), the absorptions at 1.0–2.4, 3.5–3.9, and 5.8–7.3 ppm are for the protons of the main chain, the methoxy, the benzene ring, and the hydroxyl, respectively,[5] where their area ratio is 3:3:4. In order to estimate the monomer composition in the copolymer, it is best to use the absorptions of $—OCH_3$ and $—OCH_2—$ of the side chain; that is, the relationship between the composition ratio and the area ratio as given by:

$$\frac{d[M_1]}{d[M_2]} = \frac{3A}{2B} \tag{1}$$

where $d[M_1]$ and $d[M_2]$ are the concentrations of the monomer units of M_1 (VG) and M_2 (the fluorinated monomer), respectively. A and B are the areas of the absorptions of $—OCH_3$ and $—OCH_2—$, respectively. Equation (1) is applicable for the estimation of the monomer composition present in copolymerizations. The monomer composition ratio as $F_1 = d[M_1]/(d[M_1] + d[M_2])$ at given monomer feed as $f_1 = [M_1]/([M_1] + [M_2])$ is shown in Table I.

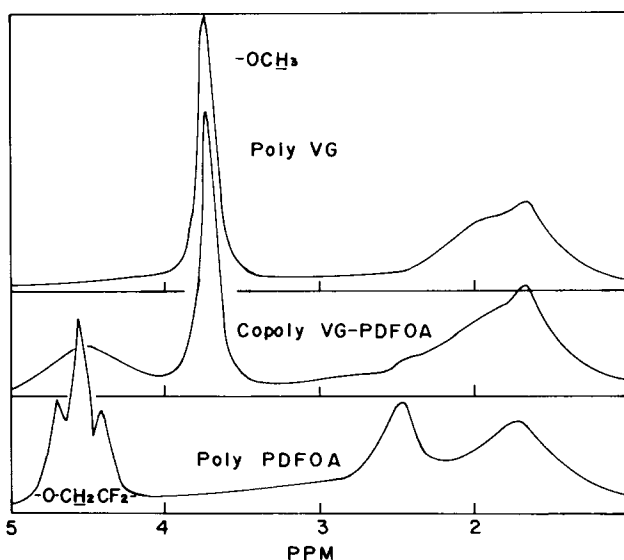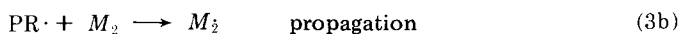The reactivity ratios in the copolymerization of VG with PDFOA are estimated
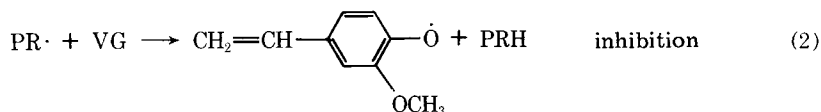
Fig. 1. ^{1}H NMR spectra of poly(VG), copoly(VG–PDFOA) ($F_1 = 0.560$), and polyPDFOA.

to be $r_1 = 0.19$ and $r_2 = 0.06$ by the Fineman–Ross method.[9]   As is apparent in Figure 2, the intercept of $f_1(F_1 - F_2)/f_1f_2$ ($f_2 = 1 - f_1$ and $F_2 = 1 - F_1$) is not precise.   Thus, the precise values are calculated to be $r_1 = 0.217$ and $r_2 = 0.0751$ by the Tidwell–Mortimer method,[10] where $r_1 = 0.19$ and $r_2 = 0.06$ are the initial values (Fig. 3).   For the other copolymerizations, the reactivity ratios are calculated by these methods (Table II).   In the copolymerization with TFEM, the copolymerizability of VG is similar to that of VP, because of $(r_1r_2)_{VG} \simeq (r_1r_2)_{VP} = 0.14$ (Table II).[8]   With OFPM, the copolymerizability of VG is similar to that of VP.   The copolymerizability of VG with PDFOA is very effective because of $r_1r_2 \ll 1$.

The copolymerization rate is given in Table I.   When $F_2 < 0.3$, R_p accelerates markedly with decreasing F_1.   The primary radical PR· yielded by the decomposition of AIBN reacts as[11]:

$$PR\cdot + VG \longrightarrow CH_2{=}CH{-}\!\!\!\left\langle\rule{0pt}{12pt}\right\rangle\!\!\!-\dot{O} + PRH \qquad \text{inhibition} \qquad (2)$$
$$OCH_3$$

$$PR\cdot + M_1 \longrightarrow M_1^{\cdot}({-}CH_2CHG) \qquad \text{propagation} \qquad (3a)$$

$$PR\cdot + M_2 \longrightarrow M_2^{\cdot} \qquad \text{propagation} \qquad (3b)$$

where $M_1^{\cdot}$ and $M_2^{\cdot}$ are the propagating radicals.   The small value of R_p for the homopolymerization of VG is explained by assuming that the rate of reaction (3a) is markedly less than that of (2).   By adding a small amount of M_2, the rate increases rapidly.   The rate constant of reaction (3b) is exceedingly larger than that of reactions (2) and (3a).   In the presence of about 30% of M_2, every primary radical reacts with M_2 and none react with VG as reactions (2) and (3a).   By further adding M_2, there may be no primary radicals, which can react with the M_2 as the surplus ($\simeq F_2 - 0.3$), and therefore the rate does not increase rapidly.

TABLE I
Copolymerization of VG with Fluorinated Monomer in Presence of [AIBN] = 0.0212 mol/liter at 60°C

$M_1 - M_2$	f_1	F_1	R_p (mol/liter hr)	$[\eta]$ (dl/g)
VG	1	1	0.023	0.066[a]
VG–TFEM	0.903	∼ 0.97	0.08	
	0.829	∼ 0.94	0.15	
	0.407	0.750	0.37	
	0.171	0.597	0.59	
	0.103	0.491	0.65	0.80[a]
VG–OFPM	0.830	∼ 0.93	0.07	0.19[a]
	0.604	0.777	0.12	0.28[a]
	0.338	0.637	0.22	0.48[a]
	0.145	0.392	0.39	1.02[a]
	0.074	0.289	0.43	1.34[a]
VG–PDFOA[c]	0.935	0.804	0.09	
	0.863	0.693	0.16	
	0.774	0.622	0.24	
	0.671	0.603	0.30	
	0.551	0.560	0.40	0.16[a]
	0.406	0.503	0.46	
	0.226	0.451	0.56	
	0.142	0.418	0.77	0.15[b]

[a] In acetone.
[b] In TCE.
[c] 50 % Acetone.

Since the reactivity of the primary radical with the fluorinated monomer is exceedingly high, VG can copolymerize with the fluorinated monomer. Furthermore, detailed discussion is not given here, because the termination rate in the copolymerization is complex and has not been sufficiently clarified.[12–14] Per-
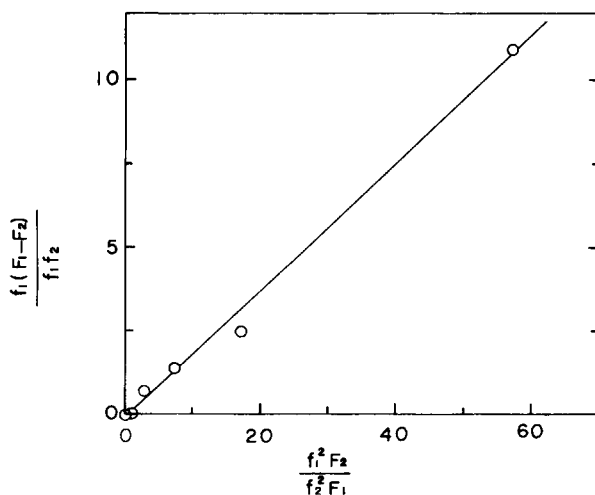

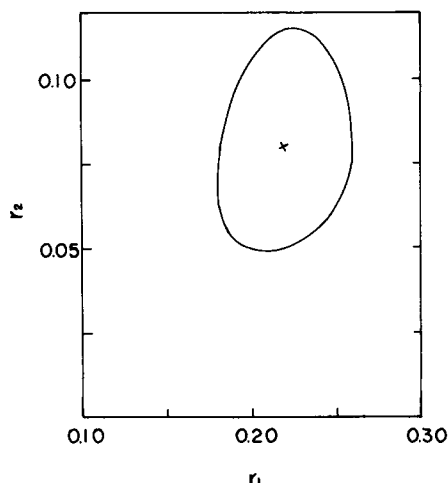Fig. 2.   Estimation of reactivity ratios for VG–PDFOA by Fineman–Ross method.[9]

Fig. 3. Joint confidence limits for reactivity ratios[10] determined for VG–PDFOA from data in copolymerization of PDFOA with VG (Table I).

TABLE II
Reactivity Ratios for Copolymerization of Fluorinated Monomer with VG and VP at 60°C

$M_1 - M_2$	r_1	r_2	$r_1 r_2$
VG–TFEM	3.2	0.050	0.16
VP–TFEM[a]	1.5	0.096	0.14
VG–OFPM	2.19	0.163	0.356
VP–OFPM[a]	1.5	0.21	0.32
VG–PDFOA	0.217	0.0751	0.0103

[a] Ref. 8.

haps, the increase in intrinsic viscosity $[\eta]$ (accordingly the molecular weight) with decreasing [VG] might be explained by assuming that the propagating radicals could react with VG by the (2)-type inhibition (Table I).

Surface Tension

Relationship between contact angle θ for water and the monomer composition in the copolymer is shown in Figure 4. The contact angles for copoly(VG–TFEM) and copoly(VG–OFPM) are 90°, which exist approximately in the range of $F_1 < 0.5$ and 0.8, respectively. For copoly(VG–PDFOA), the θ is 114° at $F_1 = 0$, and decreases slightly with increasing F_1 to become 104° when $F_1 = 0.803$. This data indicates that the water-repellent properties of copoly(VG–PDFOA) are best. The range of F_2, where the contact angle is held approximately at the θ for the respective homopolymer, will be discussed in terms of the number of fluorines contained in the M_2 unit. That is, the copolymer with TFEM containing only three fluorines holds at $\theta \simeq 90°$ in the range of $F_2 > 0.5$. That range becomes $F_2 > 0.2$ for the copolymer with OFPM containing eight fluorines. Further, the θ is still held on 104° at $F_2 = 0.197$ for that with PDFOA containing 15 fluorines.
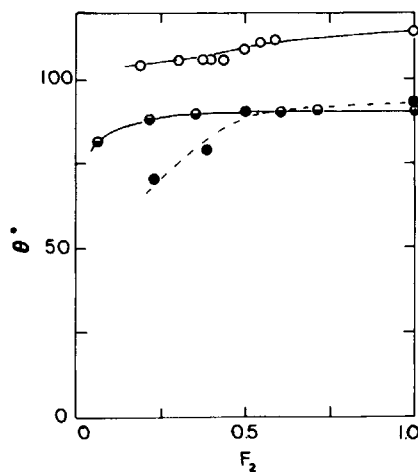
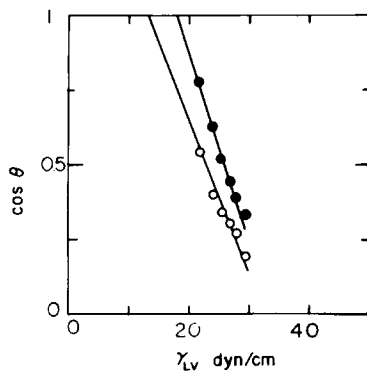Fig. 4. Contact angle of water on copolymer film: copoly(VG–TFEM), ●; VG–OFPM, ◖; VG–PDFOA, ○.

Fig. 5. Determination of critical surface tension for copoly(VG–PDFOA) of F_1 = 0.451, ○; 0.693, ●.

TABLE III
Critical Surface Tension for Copolymer

Copoly$M_1 - M_2$	F_1	C
HomopolyTFEM	0	17.9[a]
Copoly(VG–TFEM)	0.491	18.5
Homopoly(OFPM)	0	17.0[a]
Copoly(VG–OFPM)	0.392	17.8
Homopoly(PDFOA)	0	10.4[b]
Copoly(VG–PDFOA)	0.451	13.5
Copoly(VG–PDFOA)	0.693	18.6
Copoly(VP–HFiPM)	~0.1	16.5[a]

[a] Ref. 8.
[b] Ref. 16.

In order to more generally evaluate the water- and oil-repellent properties, the critical surface tension γ_C defined by Zisman[15] was determined. There is a linear relationship between surface tension γ_{LV} and cos θ, when γ_{LV} is low. The γ_C is defined as γ_{LV} when cos θ = 1 and, therefore, estimated by extending

such a line to $\cos \theta = 1$. The lines for copoly(VG–PDFOA) are shown in Figure 5. The γ_C obtained is shown in Table III. The γ_C is lower when F_1 is less. The $\gamma_C = 13.5$ dyne/cm at $F_1 = 0.392$ is close to 10.4 dyne/cm for poly(PDFOA),[16] and is less than 16.5 dyne/cm for the copolymer of VG with hexafluoroisopropylmethacrylate (HFiPM).[8] The critical surface tensions for copoly(VG–TFEM) and copoly(VG–OFPM) are also obtained and are close to the γ_C of the respective fluorinated homopolymers (Table III).

In conclusion, the copolymerization of PDFOA with VG is best. Further, the water- and oil-repellent properties of copoly(VG–PDFOA) are also superior to the other copolymers. This copolymer would provide hydrogen bonding to hydroxyapatite which contains the hydroxyl group.

APPENDIX

In enzymatic dehydrogenation,[4] the rate of abstraction from the phenol, which contains the double bond, is larger by about tenfold than that of the phenol without the double bond.[17-19] In view of this, the primary radical yielded by the decomposition of AIBN may abstract the phenolic hydrogen from VG, even if it can not abstract that from N-(3,5-di-tert-butyl-4-hydroxy) benzylacrylamide.[11]

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