

Preparation and Properties of Polymers Anchoring Biphenyl-2-ol

Tomomichi ISHIKAWA* and Satoshi ASAI

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University,
Fukasawa, Setagaya-ku, Tokyo 158

(Received December 18, 1982)

Synopsis. The monomer, 2-biphenyl acrylate (BPA), was prepared and was polymerized and copolymerized with vinyl acetate (VAc), styrene and *N*-vinylpyrrolidone. The reactivity ratios of BPA(M_1) with VAc were evaluated as $r_1=4.6+0.4$ and $r_2=0.37+0.08$. The polymers were hydrolyzed in methanol-phosphate buffer solution (pH 6 and 8), and the release rate of biphenyl-2-ol from the polymer was investigated.

Recently, there has been a great deal of interest in drugs,¹⁻³ agricultural medicines^{4,5} and coatings^{6,7} with long-lasting biological activity. Polymers of which fungicidal biphenyl-2-ol (*o*-phenylphenol, abbreviated to OPP) is anchored *via* hydrolyzable ester link to the main chain may be available to control the release of the fungicide over an extended period. Preparation of the polymers is accomplished by polymerization and copolymerization of 2-biphenyl acrylate (BPA). In this work we describe the synthesis of both the monomer and polymer, and a study of the hydrolytic release of OPP from the polymer.

Experimental

Materials. Vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP), styrene (St), and acryloyl chloride were distilled under reduced pressure prior to use. OPP and α,α' -azobisisobutyronitrile (AIBN) were purified by recrystallization. Benzene used as reaction media was dried and purified by distillation.

Synthesis of BPA. Previously dried benzene (100 cm³), OPP (34.0 g, 0.2 mol) and triethylamine (22 g, 0.22 mol) were placed in a 200 cm³ four necked round-bottom flask equipped with a stirrer, condenser and dropping funnel with a nitrogen inlet tube. The mixture was then maintained at 20–25 °C while acryloyl chloride (20.0 g, 0.22 mol) was added through the dropping funnel. Stirring was continued for additional 4 h. After the precipitate was filtered, the benzene solution was washed with 5% aqueous NaHCO₃ solu-

tion and twice with water. The benzene layer was dried over Na₂SO₄, and then the benzene was removed by vacuum evaporation. The pale yellow solution which remained was distilled under reduced pressure in the presence of 4-*t*-butylcatechol to yield 31.0 g (64.0%) BPA: bp 120–122 °C (200 Pa); IR (liquid) 1740 (C=O), 1630 (C=C), 1190, 1145 (C–O–C) cm⁻¹; ¹H-NMR (CDCl₃) $\delta=5.60, 6.25$ (3H, m, CH₂=CH) and 7.30 (9H, m, aromatic proton). Found: C, 83.43; H, 6.29%. Calcd for C₁₅H₁₂O₂: C, 83.36; H, 6.18%.

General Procedure for Polymerization. All the polymerization experiments were carried out using a bulk technique at 60 °C in the presence of 0.5 wt% AIBN. The polymers obtained were purified by repeated precipitation from a solvent system into a non-solvent system. The purified polymers were dried at 60 °C under vacuum to constant weight and submitted to elemental analysis.

General Procedure for Hydrolysis. The polymer (converted into 0.5–0.6 mmol OPP) and the phosphate buffered methanol–water solution (pH 6 or 8; 200 cm³) were placed in 300 cm³ Erlenmeyer flask, and then maintained at 30 °C with a regulated water bath. The mixture was shaken often, and a part of this mixture (1 cm³) was taken out periodically. The polymers was removed by filtration. The filtrate was diluted with the buffer solution (4 cm³). The solution was put into a cubic quartz cell (1 cm) and detection of OPP was performed by UV at 244.0 nm.

Synthesis of 2-Biphenyl Propionate (BPP). BPP was prepared from OPP with propionyl chloride by a similar procedure to that of BPA-synthesis: yield 54.0%; bp 156–158 °C (1333 Pa); IR (liquid) 1760 (C=O), 1180 and 1140 (C–O–C) cm⁻¹; ¹H-NMR (CDCl₃) $\delta=1.00$ (3H, t, CH₃), 2.30 (2H, m, CH₂) and 7.30 (9H, m, aromatic proton). Found: C, 79.46; H, 6.44%. Calcd for C₁₅H₁₄O₂: C, 79.62; H, 6.24%.

Results and Discussion

Polymerization and Copolymerization of BPA. The BPA obtained was a colorless viscous liquid. The

TABLE 1. POLYMERIZATION AND COPOLYMERIZATION OF BPA

Run	Monomer		Polymer			
	BPA (mol%)	Comonomer	Conversion %	Analysis (%)	BPA (mol%)	$[\eta]^a$ dm ³ g ⁻¹
1	20.0	VAc	23.4	C 74.34	54.3	—
2	50.0	VAc	22.4	C 77.87	77.5	—
3	80.0	VAc	24.2	C 79.74	93.9	—
4	20.0	VAc	82.0	C 66.50	22.9	0.12
5	50.0	VAc	91.6	C 73.72	51.0	0.35
6	79.7	VAc	79.8	C 77.70	76.1	0.35
7	20.0	St	76.8	C 90.32	8.26	0.37
8	50.0	St	75.7	C 84.26	48.6	0.32
9	80.0	St	72.0	C 81.04	88.1	0.34
10	50.0	NVP	78.3	N 3.46	56.7	0.26
11	80.0	NVP	79.3	N 1.81	74.7	0.37
12	100	—	81.0	—	100.0	0.03

a) Measured in benzene at 30 °C.

TABLE 2. HYDROLYSIS OF BPA POLYMER

Run	Polymer		Conversion/%			
			pH 8		pH 6	
			1 week	2 weeks	1 week	2 weeks
5	51.0	VAc	4.3	12.0	0.1	0.2
6	76.1	VAc	9.5	18.7	1.2	1.8
7	8.26	St	4.0	6.5	0.3	0.6
8	48.6	St	8.0	13.5	0.5	0.8
9	88.1	St	13.1	18.4	1.3	2.1
10	56.7	NVP	6.4	7.5	2.8	3.3
11	74.7	NVP	16.4	19.5	4.9	6.0
12	100	—	23.0	30.0	1.8	3.0

homopolymer was purified by reprecipitation from dichloromethane and methanol. Purification of the copolymers with NVP were by repeated precipitation from benzene and hexane. The copolymers with VAc or St were redissolved in dichloromethane and reprecipitated in methanol. Results are shown in Table 1. These polymers are colorless powders, soluble in organic solvents such as acetone, benzene, tetrahydrofuran and dichloromethane.

For BPA(M_1) with VAc, the reactivity ratios were determined by the integral form of the general copolymerization equation from the results for Runs 1–3 in Table 1. The r_1 and r_2 values obtained were $r_1 = 4.6 \pm 0.4$ and $r_2 = 0.37 \pm 0.08$. The conversion was calculated using Spinner and co-worker's equation⁸⁾ from these r_1 and r_2 values were fairly consistent with the results for Runs 4–6.

Release of OPP from Polymer. The polymers were hydrolyzed at pH 6 and 8. OPP released during the hydrolysis was dissolved in methanol-phosphate buffer solution(1/1 volume ratio) because of their lower solubility in water. The amount of OPP released was determined by measuring its absorbance at 244.0 nm. Table 2 shows the results after one and two weeks. It appears that the release rate of OPP are faster at pH 8 than at pH 6. After one week at pH 8, BPA-NVP copolymer was hydrolyzed faster than the other two copolymers, but much slower than the BPA homopolymer. In the period between one and two weeks, however, BPA-VAc copolymer was more susceptible to hydrolysis than the others. In this copolymer also, it was observed that the time-conversion plots are nearly linear and release the incorporated OPP by zero-order kinetics for at least two weeks.

As Table 2 shows, when the OPP content becomes higher, the conversion increases. But the BPA homopolymer was hydrolyzed very slowly and even after two weeks, about 70% of OPP unit remained on the polymer chain. In order to compare with the hydrolysis rate of the BPA homopolymer, a model compound, BPP, was hydrolyzed. The results were shown in Fig. 1. From these results, it seems that the polymers were resistant to hydrolysis and released OPP gradually. When the polymers are used as coating

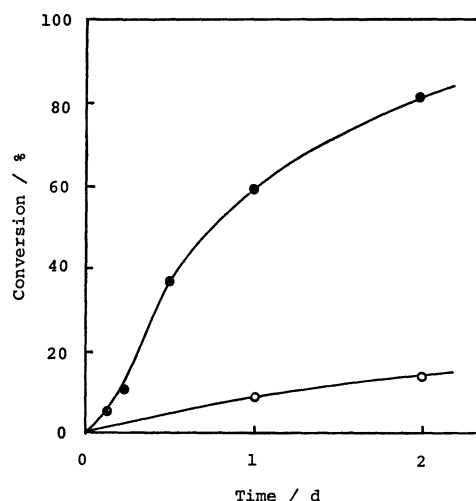


Fig. 1. Hydrolysis of BPP and BPA-homopolymer at pH 8.

●: BPP, ○: BPA-homopolymer

films, the above results suggest that the polymers will lose few OPP under a natural environment such as in the rain.

References

- 1) P. P. Umrigar, S. Ohashi, and G. B. Butler, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 351 (1979).
- 2) H. Ritter, *Makromol. Chem., Rapid Commun.*, **3**, 431 (1982).
- 3) J. Pitha, S. Zawadzki, and B. A. Hughes, *Makromol. Chem.*, **183**, 781 (1982).
- 4) M. B. Shambhu, G. A. Digenis, D. K. Gulati, K. Bowman, and P. S. Sabhrwal, *J. Agric. Food Chem.*, **24**, 666 (1976).
- 5) J. Bartulin and B. L. Rivas, *Makromol. Chem., Rapid Commun.*, **2**, 375 (1981).
- 6) C. U. Pittman, Jr., G. A. Stahl, and H. Winters, *J. Coatings Tech.*, **50**, 49 (1978).
- 7) C. U. Pittman, Jr., and G. A. Stahl, *J. Appl. Polym. Sci.*, **26**, 2403 (1981).
- 8) I. H. Spinner, B. C. Y. Lu, and W. F. Graydon, *J. Am. Chem. Soc.*, **77**, 2198 (1955).