

NOTE

Study on Polymerization of Methyl Methacrylate in Water–Solvent Mixtures

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INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a well known polymer and is characterized by its crystal clear transparency, unexcelled outdoor weatherability, outstanding surface hardness, good chemical resistance, and a combination of stiffness and moderate toughness.¹ The applications of PMMA include exterior signs, safety glazing, skylights, aircraft canopies, and lightening fixtures. PMMA molding compounds are used in the automotive industry for tail lights and in appliance panels.

MMA can be polymerized² under the influence of heat and light with or without an oxygen yielding catalyst (initiator) such as benzoyl peroxide. Polymerization is usually carried out in bulk, but for certain purposes it is desirable to carry out the reaction in solution, emulsion, or suspension. The conditions under which the polymerization takes place affect the characteristics of the product. Recent studies on polymerization of monomer in water mixed with organic solvents are gaining importance. It is believed that this method would combine the advantages of solution and suspension (in water) polymerization in a number of ways to change polymerization conditions and product properties.³ Polymerization of MMA in water,^{4–6} water–alcohol,⁷ and water–organic solvent mixtures⁸ was studied. It was found that the rate of polymerization and viscosity average molecular weight of the polymer increased when the polymerization was conducted in ethylene glycol–water mixtures. In the present study MMA was polymerized in water–acetone, water–di-

methyl formamide (DMF), and water–methanol mixtures to determine their effect on the PMMA properties.

EXPERIMENTAL

Materials

MMA monomer (Fluka AG, Switzerland), stabilized with 100 ppm hydroquinone, was washed with aqueous sodium hydroxide and then distilled water until the washings were neutral. It was then dried over anhydrous sodium sulfate. Benzoyl peroxide (BDH, Bombay), having 12% water as the stabilizer, was purified by dissolving it in chloroform at 25°C and adding it to twice its volume of methanol. When kept in a refrigerator at 10°C overnight, pure benzoyl peroxide separated out as transparent needles. It was then filtered, dried, and stored at 10°C in an air tight container. The solvents methanol, acetone, and DMF were purified according to the standard reported procedures.⁹

Solubility of Monomer in Water–Solvent Mixture

The solubility of MMA in water–acetone, water–methanol, and water–DMF was determined by adding monomer (15 mL) in water–solvent mixtures (60 mL). Both the monomer and water solvent mixtures were shaken vigorously in a graduated and stoppered measuring cylinder for 5 min. Both layers were allowed to separate clearly after 1 h at 30°C. The solubility of the monomer in the medium was also determined in the same manner at 80–85°C, the temperature at which the polymerization was carried out. The volumes of the

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Table I Solubility Data of Methyl Methacrylate (MMA) in Water–Solvent Media System: Medium (60 mL) + MMA (15 mL)

Code	Medium Composition (60 mL)		Medium—Monomer Solubility (mL)				Result
			at 30°C		at 80°C		
	Water + Solvent	Ratio (%)	Medium (mL)	Monomer (mL)	Medium (mL)	Monomer (mL)	
A	60 + 0	100 : 0	60	15	60	15	I.S.
B1	54 + 6	90 : 10	60	15	60	15	I.S.
B2	45 + 15	75 : 25	59	16	59	16	I.S.
B3	36 + 24	60 : 40	55	20	55	20	P.S.
C1	54 + 6	90 : 10	60	15	58	17	P.S.
C2	45 + 15	75 : 25	52	23	48	27	P.S.
C3	36 + 24	60 : 40	42	33	40	35	P.S.
D1	54 + 6	90 : 10	62	13	64	11	P.S.
D2	45 + 15	75 : 25	63	12	65	10	P.S.
D3	36 + 24	60 : 40	68	07	75	00	S

B, water–acetone; C, water–DMF; D, water–methanol; I.S., insoluble; P.S., partially soluble; S, soluble.

medium layer and the monomer layer were measured. The results are shown in Table I.

Determination of Surface Tension of Water–Solvent Mixtures

The surface tension of the water–solvent mixtures was determined by using a Torsion balance (White Electrical Instruments Co. Ltd., U.K.) with a ring having a circumference of 4 cm. The results are reported in Table II.

Polymerization of MMA

Distilled water and solvent (DMF, methanol, acetone) mixtures in ratios as shown in Table I (60 g) and MgCO_3 (0.6 g) were placed in a 250-mL, three neck, round-bottom flask equipped with an overhead stirrer, condenser, and dropping funnel. The round-bottom flask was kept in a water bath at a $85 \pm 5^\circ\text{C}$ temperature. MMA monomer (15 g) with the initiator benzoyl peroxide (0.15 g) was placed in the dropping funnel and added to the reaction flask slowly over a period of 2 h. The heating was further continued for 1 h more. The reaction mixture was cooled to room temperature and washed with dilute H_2SO_4 to remove the MgCO_3 as magnesium sulfate, which is soluble in water. Polymer beads were filtered through a Buchner funnel and washed with water several times until the washings were neutral pH. The polymer was dried in a vacuum oven at 50°C . The polymer was redissolved in thiophene free benzene to obtain about 2% polymer solution. The

polymer was then precipitated by the addition of this polymer solution in vigorously stirred methanol for about 30 min. The precipitated polymer powder was filtered through a Buchner funnel and dried at 90°C until constant weight was obtained. The percentage yield was determined gravimetrically.

Determination of Molecular Weights of PMMA by GPC

Number and weight average molecular weights (M_n , M_w) of PMMA and their polydispersity were studied

Table II Surface Tension of Water–Solvent Mixtures

Code	Water–Solvent Mixtures	Surface Tension (dyne/cm)	
A	Water	72.0	
B1	Water–acetone	90 : 10	51.5
		75 : 25	41.5
		60 : 40	35.5
C1	Water–DMF	90 : 10	56.0
		75 : 25	46.0
		60 : 40	44.0
D1	Water–methanol	90 : 10	48.0
		75 : 25	38.0
		60 : 40	29.2

using a GPC Shimadzu LC6A model equipped with a refractive index detector. The columns used were polystyragel having exclusion limits of 10^4 , 10^7 , and 500 \AA and were connected in series. The flow rate was maintained at 1 mL/min using tetrahydrofuran as eluent. Five monodisperse polystyrene standards supplied by Shimadzu were used for the calibration. M_n , M_w , and molecular weight distribution (MWD) values for each polymer are given in Table III.

Determination of Intrinsic Viscosity

A 0.1% (w/w) solution was prepared by dissolving the required amount of polymer in a solvent such as benzene or methyl ethyl ketone (MEK) and storing in a room conditioned at $25 \pm 1^\circ\text{C}$ for at least 24 h. The homogeneous PMMA solution was filtered to make it free from any suspending particles. It was weighed again to check for the weight loss, due to the evaporation of solvent just before conducting the viscosity measurements at $25 \pm 1^\circ\text{C}$. An Ubblohde Schott Gerrate dilution viscometer with an automatic recorder and thermostat was used for the viscosity measurements. Five consecutive flow times in seconds, which agreed within at least ± 0.2 s, were recorded for each polymer solution. The average flow time in seconds was used for calculating the limiting viscosity number or intrinsic viscosity. No kinetic energy corrections were made because the efflux flow times of the solvents were more than 100 s. Because intrinsic viscosities of the polymer solutions are below 2.0 dL/g, the effect of shear rate was negligible. The intrinsic viscosities in two different solvents (benzene and MEK) were calculated from the following relation¹⁰:

$$\log[\eta] = \log\left(\frac{\eta_{sp}}{C}\right) + K\eta_{sp} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, η_{sp} is the specific viscosity, C is the concentration (g/dL), and K is the constant, Huggin's coefficient (0.14 for $\eta_{sp} < 0.3$).

The viscosity average molecular weights (M_v) of the polymers were calculated from the corresponding $[\eta]$ values by using the following Mark-Houwink relation:

$$[\eta] = KM_v^\alpha \quad (2)$$

where K and α are specific to respective polymer solutions.

Table III Yields, Molecular Weights, and Polydispersities of Poly(methyl methacrylate)

Polymer	Yield (%)	M_w	M_n	MWD
A	85	276246	205424	1.34
B1	82	279290	213037	1.31
B2	74	310468	255043	1.22
B3	70	90476	86707	1.04
C1	76	201087	128684	1.56
C2	72	237198	153060	1.55
C3	63	383845	261242	1.36
D1	85	303636	238923	1.25
D2	82	373188	264680	1.41
D3	78	122062	95959	1.26

RESULTS AND DISCUSSION

From the solubility data (Table I) it is observed that in water-methanol solvent medium (D series) the monomer goes into the medium and hence the top monomer layer is reduced with the increase of the methanol content in the medium. But in water-DMF solvent medium (C series) the DMF goes into the monomer layer and is found to increase with the increase in the DMF content in the medium. Similar observations were also noticed in water-acetone solvent medium (B series) but to a lesser extent.

The polymerization of MMA in water-acetone, water-DMF, and water-methanol mixtures showed the characteristics of heterogeneous polymerization. The reaction system was heterogeneous in most of the cases except in D3 (water-methanol, 60 : 40) when the monomer was completely soluble at 80°C . However, as the polymerization is proceeding the polymer separates as fine powder due to its insolubility in the water-solvent medium. Due to the partial solubility of monomer in the medium of polymerization, the suspension and solution polymerizations take place simultaneously. The monomer solubility increased in the polymerization medium by the increase in the addition of organic solvent content (Table I), which regulated the rate of polymerization and product properties due to the occlusion level of growing chain radicals.

The data of molecular weights and polydispersity index are reported in Table III. They (M_w) are in the range of 90,476–310,468 and 1.04–1.56, which indicated that most of the homopolymers have narrow MWD. The unusual narrow MWD of the polymer may be due to the small amount of low molecular weight polymers lost during the purification technique. The effects of solvent medium on MWD of these polymers is not very significant.

The maximum yield (85%) of PMMA was obtained when MMA was polymerized in water alone. When the

polymerizations are conducted in water–solvent systems, the yield of the polymer reduces in the following order (Table III):

$$A > (D1, D2, D3) > (B1, B2, B3) > (C1, C2, C3)$$

Also, when the solvent content in the polymerization medium is increased, the yields of the polymer also reduced as indicated below.

$$B1 > B2 > B3; \quad C1 > C2 > C3; \quad D1 > D2 > D3$$

This may be explained by the chain transfer mechanism and biradical termination, especially at a higher concentration of solvent in the medium of polymerization. This can be proved further on the basis of chain transfer coefficients. The chain transfer coefficients of methanol, acetone, and DMF are 0.33, 1.10, and 2.42, respectively. Therefore, these chain transfer coefficients have influence on the yields of the polymers. The yields thus obtained in the water–methanol medium are higher than those obtained in water–acetone and water–DMF systems.

$$D1 > B1 > C1; \quad D2 > B2 > C2; \quad D3 > B3 > C3$$

The surface tensions of water–solvent mixtures were determined and are reported in Table II. The surface tension of three media of polymerization has effect on the polymerization of MMA. The surface tension of water–methanol mixtures is lower than water–acetone mixtures and water–DMF mixtures. The surface tension of the medium helps in establishing the initial monomer droplet size distribution, controls droplet coalescence, and reduces particle agglomeration. Therefore, this is also one of the reasons for obtaining high yields of PMMA with high M_w and M_n in water–methanol systems. The yields and the molecular weights of PMMA are the lowest in the water–DMF system because the system has the highest surface tension of all the systems tried in this work.

Viscosity Studies

The viscosity of dilute PMMA solutions (0.1%) in benzene and MEK have been determined. The intrinsic viscosities $[\eta]$ and viscosity average molecular weights are reported in Table IV. In benzene it is observed that the intrinsic viscosity of polymer A is less than all other polymers polymerized in different water–solvent media. It is also observed in all the cases that the intrinsic viscosity of PMMA in benzene is higher than in MEK. Therefore, it can be concluded that the benzene is a better solvent for PMMA than MEK. A good solvent (benzene) is one in which polymer segments prefer con-

Table IV Intrinsic Viscosity and Viscosity Average Molecular Weights of PMMA

Polymer	Solvent	$[\eta]$ (dL/g)	M_v
A	Benzene	1.233	27,589
	MEK	0.989	24,696
B1	Benzene	1.496	35,581
	MEK	0.899	21,631
B2	Benzene	1.797	45,288
	MEK	1.226	33,281
B3	Benzene	1.370	38,831
	MEK	1.372	31,752
C1	Benzene	1.287	29,190
	MEK	0.816	18,908
C2	Benzene	1.512	36,082
	MEK	0.990	24,730
C3	Benzene	1.523	36,152
	MEK	1.118	30,734
D1	Benzene	1.752	43,801
	MEK	1.342	37,734
D2	Benzene	2.311	63,057
	MEK	1.579	47,296
D3	Benzene	1.847	46,952
	MEK	1.200	32,305

The values of K and a of PMMA in: benzene, $K = 5.2 \times 10^{-4}$ dL/g, $a = 0.76$; MEK, $K = 6.8 \times 10^{-4}$ dL/g, $a = 0.72$.

tacts with the solvent molecules and the polymer expands or swells in solution as opposed to a poor solvent (MEK) in which the polymer segments prefer contacts with their own kind and thereby the polymer molecules tend to coil up and minimize the volume of the solution it occupies. A good solvent for a polymer is one in which the residual chemical potential is a minimum. In such a system the intrinsic viscosity has maximum value.

The viscosity average molecular weights of the PMMA prepared in water–methanol medium are higher than those made in water–acetone medium. The viscosity average molecular weights of PMMA prepared in water–DMF are the lowest. These results are in agreement with weight average and number average molecular weights obtained.

CONCLUSIONS

It is concluded from this study that the properties of the polymers can be varied by varying the medium in which the polymerization is conducted. The water–solvent systems are good polymerization media because they combine the advantages of solution and suspension polymerizations. The surface tension of the media

also contributed to the polymer properties apart from the chain transfer coefficients of the solvents used in the media of polymerization. Therefore, the PMMA obtained from the polymerization of MMA in water-methanol medium has high M_w , M_n , and M_v because methanol has the lowest surface tension and low chain transfer coefficients. The water-DMF medium gave the PMMA with the lowest M_w , M_n , and M_v because DMF has high surface tension and a high chain transfer coefficient.

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