

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

p-Cumylphenyl Methacrylate: Synthesis, Polymerization, And Copolymerization

C. V. Bindushree^a; B. Venkataramanan^a; R. S. Khisti^a; S. Sivaram^a

^a Division of Polymer Chemistry, National Chemical Laboratory, Pune, India

To cite this Article Bindushree, C. V. , Venkataramanan, B. , Khisti, R. S. and Sivaram, S.(1998) 'p-Cumylphenyl Methacrylate: Synthesis, Polymerization, And Copolymerization', *Journal of Macromolecular Science, Part A*, 35: 1, 183 – 191

To link to this Article: DOI: 10.1080/10601329808001970

URL: <http://dx.doi.org/10.1080/10601329808001970>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

p-CUMYLPHENYL METHACRYLATE: SYNTHESIS, POLYMERIZATION, AND COPOLYMERIZATION

C. V. Bindushree, B. Venkataramanan,

R. S. Khisti, and S. Sivaram*

Division of Polymer Chemistry

National Chemical Laboratory

Pune 411 008, India

ABSTRACT

A new methacrylic monomer from the reaction of methacryloyl chloride with p-cumylphenol has been synthesized. The effect of sterically bulky p-cumylphenyl group on homopolymerization and copolymerization was examined. In copolymers, p-cumylphenyl methacrylate increases the T_g of acrylic polymers. The T_g of the copolymers as determined by DSC agrees with both the Flory-Fox and Gordon-Taylor relationships.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is known for its glass-like transparency, good mechanical properties and easy processability. However, in many cases, applications of PMMA are limited by its low glass transition temperature ($T_g \sim 105^\circ\text{C}$).

Among the many strategies available for increasing the T_g of methacrylate polymers, the most promising is the replacement of the methyl group in the ester part of the monomer. Sterically hindered and conformationally rigid cycloalkyl groups cause a significant increase in T_g . For example, T_g varies from 110°C for poly(cyclohexyl methacrylate) [1], to 194°C for poly(bornylmethacrylate) and 200°C for poly(isobornyl methacrylate) [2]. Similarly, an increase in polarity of the

ester group causes an increase in T_g , which is observed in 4-cyanophenyl methacrylate (T_g 155°C) [3].

p-Cumylphenol [4-(2-phenyl isopropyl)phenol] is a readily available industrial chemical whose ester with methacrylic acid could result in an interesting acrylic monomer with sterically bulky side chain group. It is therefore of interest to study the T_g behavior of polymer derived from such a monomer.

In this paper, we wish to report the synthesis of a new methacrylic monomer derived from the reaction of methacryloyl chloride with p-cumylphenol as well as its homopolymerization and copolymerization behavior.

EXPERIMENTAL

Materials

p-Cumylphenol [4-(2-phenyl isopropyl)phenol], (m.p. 98-100°C) supplied by Herdillia Chemical, (Thane, India), was purified by recrystallization from petroleum ether. Methyl methacrylate (MMA) and methacrylic acid (Aldrich Chemicals, USA) were dried over calcium hydride and distilled under nitrogen. Benzoyl chloride was supplied by S. D. Fine Chemicals, India. Triethylamine (Sisco Research Lab, India) and hydroquinone (Loba Chemie, India) were used without any further purification. Tetrahydrofuran (THF) and toluene were distilled and dried over Na-benzophenone ketyl.

Measurements

FTIR spectra were recorded on a Perkin-Elmer 16PC-FTIR instrument. ^1H NMR spectra were recorded on a Bruker 200 MHz NMR spectrometer in CDCl_3 . Melting points (uncorrected) were determined in open capillary tubes using a melting point apparatus (Cambell Electronics, India). The inherent viscosity of 1% (w/v) solution of polymer in chloroform was determined at 30°C using an automated (Schott Gerate AVS 440, Germany) Ubbelohde viscometer. Differential scanning calorimetry was performed on a Perkin Elmer DSC-7 in aluminium pans at a heating rate of 20°C/min under nitrogen atmosphere. The sample was heated upto 250°C, cooled to room temperature and the T_g was recorded during the second heating run. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 at a heating rate of 10°C/min.

Monomer Synthesis

Methacryloyl chloride was prepared by reacting methacrylic acid with benzoyl chloride using the reported procedure. p-Cumylphenyl methacrylate was

synthesized as follows: a mixture of p-cumylphenol (0.04 mol) in 20 mL THF and triethylamine (0.04 mol) was taken in a two-neck round bottom flask equipped with a magnetic stirrer, thermometer, and dropping funnel, and then cooled to 0°C. To this was added methacryloyl chloride (0.04 mol) in THF dropwise, maintaining the temperature at 0-5°C. After complete addition of methacryloyl chloride, the reaction was continued for a further period of 1 hour. The reaction mixture was transferred to a separating funnel, washed sequentially with distilled water, 5% NaOH solution and water. The solvent was evaporated and the resulting monomer purified by column chromatography (neutral alumina), using petroleum ether as elutant. (yield~80%). IR, (nujol, cm^{-1}), ester carbonyl C=O 1740, olefinic CH_2 band, 1630-1420, ^1H NMR (δ , CDCl_3), 7-7.2 (m, 2H, aromatic) and 7.3-7.5 (m, 7H, aromatic), 5.5-6.5 (m, 2H, olefinic), 2.3 (s, 3H, CH_3), 1.7 (s, 6H, 2CH_3 between phenyl rings).

Polymerization

Free radical polymerization was carried out in a sealed tube in the presence of benzoyl peroxide as an initiator in dioxane at $80 \pm 2^\circ\text{C}$ for various intervals of time. The resulting polymer was isolated by precipitating in methanol and dried under vacuum for 24 hours. ^1H NMR (δ , CDCl_3), 7-7.2 (m, 2H, aromatic) and 7.3-7.5 (m, 7H, aromatic), 2.3 (d, 2H, CH_2), 1.7 (9H, 3CH_3).

Copolymerization

The copolymerization of p-cumylphenyl methacrylate with MMA using different mole % of p-cumylphenyl methacrylate was carried out in a sealed tube at $80 \pm 2^\circ\text{C}$ in dioxane solution for 15 hours. For estimating monomer reactivity ratios, copolymerization experiments were terminated at less than 2% conversion. The resulting copolymers were purified by dissolving in dioxane and reprecipitation from methanol. The composition of the copolymers were determined by ^1H NMR, [4] (Figure 1).

RESULTS AND DISCUSSION

The polymerization of p-cumylphenyl methacrylate (CPMA) was performed in dioxane at different monomer to initiator ratios performed (Table 1). The molecular weight of the resulting polymer increased with decreasing initiator concentration.

A homopolymer of CPMA with an inherent viscosity of 0.5 dL/g and T_g of 135°C could be readily obtained. The effect of sterically bulky ester substituent

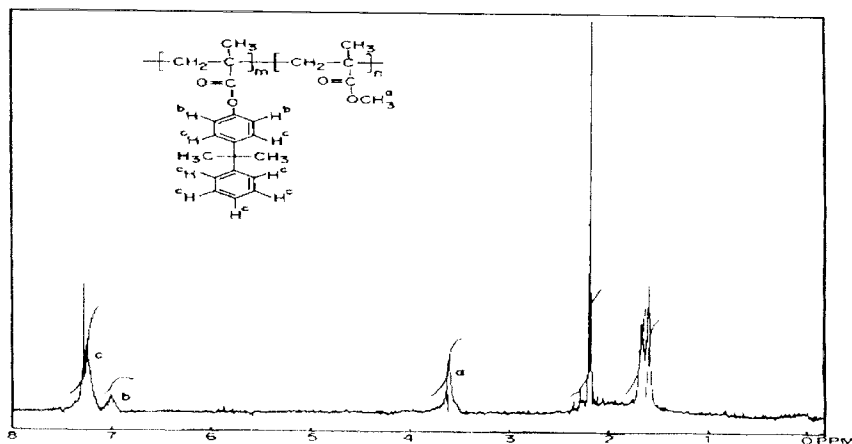


Figure 1. ^1H NMR of poly (MMA-co-CPMA)

TABLE 1. Homopolymerization of p-Cumylphenyl Methacrylate (CPMA)^a

No	Monomer [M]	Benzoyl peroxide [M], $\times 10^3$	Initiator: Monomer ratio, $\times 10^3$	Time, h	Conv, %	η_{inh} , dL/g	T_g , $^{\circ}\text{C}$
1	0.833	11	13.2	12	100	0.18	109
2	0.357	35.5	99	15	100	0.18	112
3	0.892	8.8	9.9	15	100	0.19	113
4	0.892	5.4	6.1	15	100	0.32	126
5	0.892	2.7	3.0	15	100	0.28	131
6	0.892	1.3	1.5	15	92	0.33	133
7	0.892	0.6	0.75	15	84	0.51	136

a: Polymerization was carried out in dioxane at $80 \pm 2^{\circ}\text{C}$.

TABLE 2. Copolymerization of p-Cumylphenyl Methacrylate (M_1) with Methyl Methacrylate Monomer (M_2)

No	Mole fraction (feed)		Mole fraction (copoly.) (by NMR)		Weight (g)		Benzoyl peroxide $[M], 10^4$	η_{inh} dL/g	Conv %	T_g by DSC $^{\circ}C$	T_g (calcd) using Fox-Flory equation $^{\circ}C$	T_g (calcd) using Gordon-Taylor equation $^{\circ}C$
	M_1	M_2	M_1	M_2	W_1	W_2						
1	15	85	15	85	0.35	0.7	14.2	0.93	79	124	119	124
2	20	80	20	80	0.39	0.57	13.3	0.94	82	121	120	125
3	30	70	28	72	0.56	0.46	12.4	0.90	81	126	125	126
4	40	60	40	60	0.72	0.3	12.04	0.83	83	127	126	131
5	50	50	50	50	0.75	0.26	10.02	0.72	80	129	128	132
6	70	30	70	30	0.84	0.13	8.02	0.70	79	131	132	134
7	80	20	80	20	0.93	0.079	7.5	0.66	80	135	133	135
8	90	10	90	10	0.96	0.03	7.1	0.68	84	136	135	136

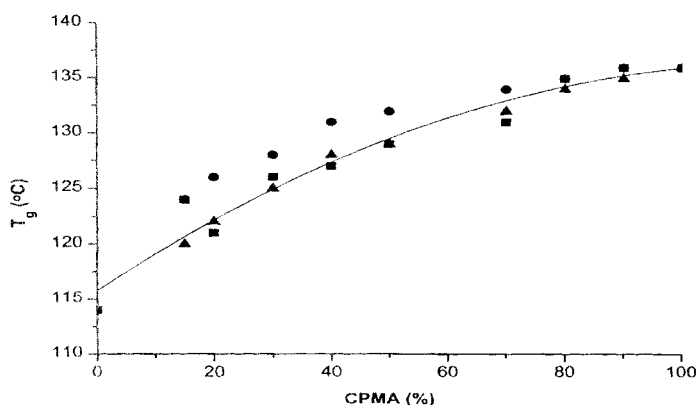
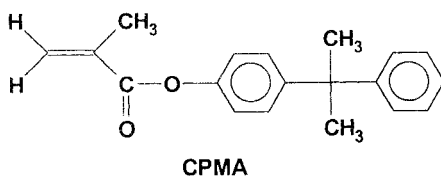


Figure 2. Dependence of T_g on mole % of CPMA ■ experimental values, ● calculated using Gordon-Taylor equation, ▲ calculated using Fox-Flory equation

on T_g is clearly observed. The higher T_g is a result of the inhibition of free rotation of the chain segments by the *p*-cumylphenyl side group. The T_g of PMMA of a similar η_{inh} is 100°C , whereas T_g of poly(phenyl methacrylate) is 110°C ($\eta_{inh} = 0.24$) [5].



The copolymerization behavior of CPMA was studied with MMA as the second comonomer. The results are shown in Table 2.

The T_g 's of the copolymers were determined by DSC. The T_g 's were calculated using the Fox-Flory [6] and Gordon-Taylor [7] equations. The Gordon-Taylor equation was linearized using the relationship:

$$T_g - T_{gA} = C (T_{gB} - T_g) w_A/w_B$$

Where: $T_{gA} = T_g$ of MMA, $T_{gB} = T_g$ of CPMA, $w_A =$ weight fraction of MMA, $w_B =$ weight fraction of CPMA, C is a crosspoint which is obtained by a plot of $T_g - T_{gA}$ vs $(T_{gB} - T_g) (w_A/w_B)$ through linear regression. The T_g was calculated using the fitting parameter, $C = 1.85$.

TABLE 3. Determination Of Reactivity Ratio Of Copolymer By Kelen-Tudos Method^a

No	Monomer Composition		Copolymer composition		% Conversion		$X=M_1/M_2$	$Y=m_1/m_2$	$G=X(Y-1)/Y$	$F=X^2/Y$	$\eta=G/\alpha+F$	$\xi=F/\alpha+F$
	M_1	M_2	m_1	m_2	CPMA	MMA						
1	80	20	73	27	0.86	1.37	4	2.7	2.5	5.92	0.384	0.91
2	70	30	73	27	1.24	1.16	2.3	2.7	1.44	1.95	0.566	0.77
3	50	50	50	50	1.84	1.84	1	1	0	1	0	0.63
4	40	60	47	52	1.89	1.41	0.6	0.9	-0.06	0.4	-0.061	0.40
5	30	70	36	64	3.14	2.53	0.42	0.56	-0.33	0.31	-0.369	0.34
6	20	80	19	81	1.45	1.21	0.25	0.23	-0.83	0.07	-0.973	0.31
7	10	90	18	82	2.1	1.42	0.11	0.21	-0.40	0.05	-0.638	0.07

^a Copolymerization was carried in dioxane at $80 \pm 2^\circ\text{C}$ for 10 min.

M_1 = Mole ratio p-cumylphenylmethacrylate

M_2 = Mole ratio of Methylmethacrylate.

m_1 = mole ratio of p-cumylmethacrylate in copolymer.

m_2 = mole ratio of methylmethacrylate in copolymer.

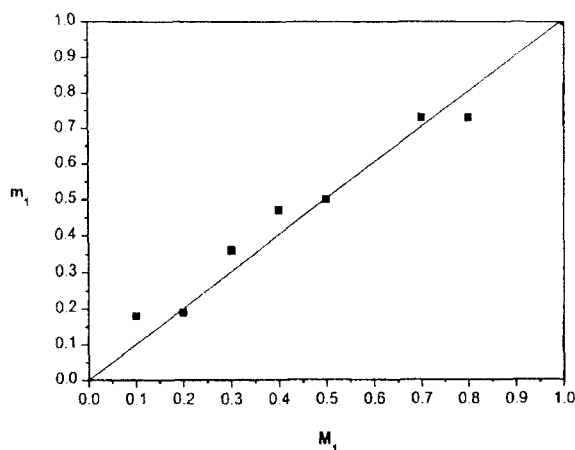


Figure 3. Plot of mole fraction of CPMA in copolymer (m_1) by NMR vs mole fraction of CPMA in feed (M_1)

The T_g 's calculated by Gordon-Taylor and Fox-Flory equations were in good agreement with the experimentally observed values (Figure 2).

The reactivity ratios for the copolymerization of CPMA(M_1), with MMA(M_2), using low conversions (>5%) was evaluated by the method of Kelen-Tudos [8] using the data shown in Table 3. The values were found to be $r_1(\text{CPMA}) = 0.637 \pm 0.147$ and $r_2(\text{MMA}) = 0.43(0.25)$ ($r_1 \cdot r_2 = 0.27$).

The plot of monomer feed ratio and the copolymer composition (Table 3) determined by ^1H NMR is linear passing through the origin indicating almost azeotropic behavior (Figure 3). The copolymer is random in nature.

CONCLUSIONS

A significant increase in T_g of PMMA is observed when the methyl group in the ester carbonyl of the methacrylate is substituted by a sterically bulky cumyl phenyl group. The T_g of the copolymers showed a gradual increase with an increase in the mole % of CPMA. The reactivity ratios of monomers have been determined by the Kelen-Tudos method. The experimentally observed T_g of the copolymers agrees reasonably well with those the values obtained using the Gordon-Taylor and Fox-Flory equations.

ACKNOWLEDGEMENTS

We thank the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, for the award of a summer research fellowship to B. Venkataramanan, and Herdillia Chemicals, Thane, for providing generous samples of p-cumylphenol.

REFERENCES

- [1] N. Hadjichristidis, C. Touloupis, and L. Fetters, *Macromolecules*, *14*, 128 (1981).
- [2] A. Matsumoto, K. Mizuta, and K. Otsu, *J. Polym. Sci., Part A, Poly. Chem. Ed.*, *31*, 2531 (1993).
- [3] G. Pizzirani, P. J. Magagnini, and P. Giusti, *J. Polym. Sci., A-2*, *9*, 1133 (1971).
- [4] W. M. Ritchey and L. E. Ball, *J. Polym. Sci. B4*, 557 (1966).
- [5] S. L. Malhotra, L. Minh, and L. P. Blanchard, *J. Macromol. Sci., Chem., A-19 (7)*, 967 (1983).
- [6] T. G. Fox, *Bull. Am. Phys. Soc.*, *1*, 123 (1956).
- [7] M. Gordon and S. J. Taylor, *J. Appl. Chem.*, *2*, 493 (1952).
- [8] T. Kelen and F. Tudos, *J. Macromol. Sci. Chem., A-9 (1)*, 1 (1975).

Received July 7, 1997

Revision received September 14, 1997