Kinetics and Thermal Analysis of Copolymerization of *m*-Isopropenyl– α , α' -Dimethylbenzyl Isocyanate with Styrene

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ABSTRACT: The copolymerizations of *m*-isopropenyl– α, α' -dimethylbenzyl isocyanate (*m*-TMI) with styrene (STY) was investigated. The weight conversion of the copolymerization reaction increased as the duration of copolymerization increased. The reaction temperature was maintained between 60 and 75°C. Molecular weights of the copolymers decreased with increasing molar fraction of *m*-TMI in the feed. This study obtained reactivity ratios, Alfrey–Price parameters, Mark–Houwink constant, characteristic ratio, thermal degradation activation energy, difference of reactive propagation activation energy, and intrinsic viscosity for the copolymers. The copolymers were characterized by using elemental analysis (EA), gel permeation chromatography, thermogravimetric analysis, and differential scanning calorimetry. The copolymer chains in solution were observed to have a high degree of stiffness and a lack of rotational freedom. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2763–2770, 1999

Key words: copolymerization; *m*-TMI; reaction kinetics; thermal analysis

INTRODUCTION

Most organic polymers require protection against heat, light, or high-energy radiation and mechanical stress.¹ Among the commercially available light stabilizers, *m*-TMI derivatives have gained most interest.² With its dual functionality, *m*-TMI allows both polymerization at the isopropenyl group and nucleophilic attack at the isocyanate group. It has also been reported to be a versatile compound for polymer synthesis,^{3,4} as well as an intermediate for the preparation of a polymerizable monomer with pendant functionality.⁵ However, *m*-TMI has no tendency to homopolymerize by a radical mechanism,⁶ and radiation grafting on its own to polymer compound is difficult. However, *m*-TMI can copolymerize with different monomers, including styrene and acrylates. In this work, we report the radical copolymerization of *m*-isopropenyl– α , α' -dimethylbenzyl isocyanate (*m*-TMI) with styrene (STY) in addition to discussing their reaction kinetics and thermal properties.

EXPERIMENTAL

Materials

m-Isopropenyl– α , α' -dimethylbenzyl isocyanate (*m*-TMI; from Aldrich of USA), tetrahydrofuran (THF; from TEDIA of USA), styrene (STY; from Janssen of Belgium), and azobis(isobutyronitrile) (AIBN; from TCI of Japan) were obtained from the indicated suppliers; other chemicals were all of reagent grade.

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Analytical Equipment

Gel permeation chromatography analysis was carried out with an instrument (Shimadzu Model 10-AD) equipped with a refractive-index detector (Shimadzu, RID-10A). The measurement was performed in a polymer-THF solution (15 mg/10 mL) at a flow rate of 1.0 mL/min at 40°C. Approximate calibration of the columns was accomplished with polystyrene standards with a narrow range of molecular weight (Waters Associates). Thermal analysis was measured at 10°C/min, 60 mL N₂/min for the thermogravimetric analysis system (TGA) (Du Pont 910) and at 20°C/min, 60 mL N₂/min for the differential scanning calorimetry (DSC) calorimeter (Du Pont 951). Elemental analysis was done for C, H, and N (Perkin–Elmer 2400). The incorporated content of m-TMI in the copolymer was determined by the mass fraction of nitrogen.

Viscometric Measurements

An Ubbelohde-type viscometer was employed to measure the flow duration of polymer solution in THF. The bath temperature was controlled at 25 \pm 0.02°C. The highest concentrations were approximately 3×10^{-2} g/mL. Values of the intrinsic viscosity [η], Huggins constant ($k_{\rm H}$), and Kraemer constant ($k_{\rm K}$) were estimated according to the Huggins equation ($\eta_{\rm red} = [\eta] + k_{\rm H}[\eta]^2 C$)⁷ and Kraemer equation ($\eta_{\rm inh} = [\eta] + k_{\rm K}[\eta]^2 C$)⁸ using the least-squares regression method, with simultaneous extrapolation to infinite dilute solution of $\eta_{\rm red} = \eta_{\rm sp}/C$ and $\eta_{\rm inh} = (1/C)\log \eta_{\rm rel}$ versus *C*, where *C* represents the concentration and $\eta_{\rm sp}$ and $\eta_{\rm rel}$ are the specific and relative viscosities.

Kinetic Measurement of Copolymerization of *m*-TMI with Styrene

m-TMI, STY, and AIBN were added to eight thick-walled test tubes. The tubes were flushed several times with dry nitrogen in an ice bath, stoppered with rubber serum caps, and placed in an oven heated to a predetermined temperature. During the reaction, an aliquot was withdrawn from the oven at a selected time interval. The gels were dissolved in dichloromethane (10-15 mL) and filtered to remove insoluble material. The solution was added dropwise to methanol to precipitate the copolymer. The copolymer was filtered, dissolved in dichloromethane, and reprecipitated several times. The material was dried and submitted for analysis to determine the *m*-TMI content of the various copolymers.



RESULTS AND DISCUSSION

Copolymerization proceeds by free-radical reactions of *m*-isopropenyl– α, α' -dimethylbenzyl isocyanate (*m*-TMI) with styrene (STY) using AIBN as initiator, as shown in Scheme 1. Nine kinds of copolymers were synthesized to the mole ratios of STY–*m*-TMI of 9/1, 7/1, 5/1, 3/1, 1/1, 1/3, 1/5, 1/7, and 1/9, as discussed below.

Effect of Copolymerization Time

Figure 1 shows the effect of reaction duration on the weight conversions of copolymerizations, molecular weights of the copolymers, and the contents of m-TMI in the copolymers. Because the weight conversions of copolymerizations for the range of STY-m-TMI = 1/3 to 1/9 were below 15% in Figures 1-3, the effects of copolymerization time, temperature, and monomer concentration were small. Hence, these copolymers are not discussed in these sections. The degree of polydispersity (M_w/M_n) , weight conversion of copolymerizations, and molecular weights of the copolymers increased with increasing reaction time. The degrees of polydispersity were between 2 and 4 for various mole ratios of STY/m-TMI. The comparison of molecular weights and weight conversions of the copolymers for STY/m-TMI is 9/1 > 7/1> 5/1 > 3/1 > 1/1. A greater weight conversion and molecular weight was observed when the reaction was prolonged beyond 30 h. Therefore, these copolymerizations rates are relatively slow. Figure 1(d) is a plot of content of *m*-TMI in the copolymer versus reaction time for various mole ratios of STY to *m*-TMI. The content of *m*-TMI in the copolymer is independent of the reaction time.

Effect of Reaction Temperature

The plot of reaction temperature versus the degree of polydispersity, the molecular weights of the copolymers, the weight conversions of copolymerizations, and the content of m-TMI in the copolymer is shown in Figure 2. The degree of



Figure 1 Effect of reaction time on the (a) degree of polydispersity, (b) molecular weight of the copolymer, (c) conversion, and (d) *m*-TMI in copolymer. (60°C; AIBN, 2 wt %; *m*-TMI, 0.1 mmol.) STY-*m*-TMI = (\bigcirc) 9/1, (\bigcirc) 7/1, (\triangle) 5/1, (\bigtriangledown) 3/1, and (\diamond) 1/1.

polydispersity of the copolymers were increased with an increasing reaction time for STY-*m*-TMI = 5/1, 7/1 and 9/1. The degrees of polydispersity are between 2 and 6 for various ratios of STY-m-TMI at various temperatures. The molecular weight of the copolymer is unsuitable for high temperature. The relative of molecular weights of the copolymers for STY–*m*-TMI is 9/1 > 7/1 > 5/1 > 3/1> 1/1. The weight conversions of the copolymers for STY-m-TMI = 3/1, 5/1, 7/1 and 9/1 under variedtemperature are consistent and is larger than that for STY-*m*-TMI = 1/1. The reactivity of copolymerization for STY-m-TMI = 1/1 was small. The weight conversions of the reactions exceeded 80% when the reaction temperature was about 60°C. The maximum value of weight conversion of copolymerization and molecular weight of the copolymer occurred at reaction temperature 60°C for all experimental runs operated under varied conditions.

When the temperature was above 75°C, the weight conversion of copolymerizations and molecular weights of the copolymers decreased. Therefore, the reaction temperature was set at 60°C to investigated the reaction kinetics. According to Figure 2(d) the content of *m*-TMI in the copolymer for varied mole ratios of STY–*m*-TMI is independent of the reaction temperature.

Effect of Monomer (m-TMI) Concentration

Varied concentrations of *m*-TMI in the feed influenced the composition of the copolymers and revealed the different characteristics of the copolymers. According Figure 3(a); the amount of *m*-TMI incorporated into the copolymer seemed not to affect the degree of polydispersity (\bar{M}_w/\bar{M}_n) ; rather, it affected \bar{M}_w and \bar{M}_n individually. The



Figure 2 Effect of reaction temperature on the (a) degree of polydispersity, (b) molecular weight of the copolymer, (c) conversion, and (d) *m*-TMI in copolymer. (60°C; reaction time, 36 h; AIBN, 2 wt %; *m*-TMI, 0.1 mmol.) STY/*m*-TMI = (\bigcirc) 9/1, (\square) 7/1, (\triangle) 5/1, (\bigtriangledown) 3/1, and (\diamond) 1/1.

degrees of polydispersity are located between 2 and 4 for various ratios of STY-m-TMI. Figure 3(b) and (c) show that the molecular weight of the copolymers and the weight conversion of copolymerization decreased as the concentration of m-TMI in the feed was increased. The order of the weight conversions of the reactions and the molecular weights of the copolymers for STY-*m*-TMI are 9/1 > 7/1 > 5/1 > 3/1 > 1/1. Increasing the proportion of m-TMI in the feed resulted in smaller molecular weights [Fig. 3(b)]. Therefore, *m*-TMI may very probably act as a chain-terminating or chain-transfer agent. Figure 3(d) is the plot of *m*-TMI levels in the copolymer versus the molar fraction of *m*-TMI in the feed. According to the experimental results, the content of *m*-TMI in the copolymer is nearly proportional to the molar fraction of m-TMI in the feed. The molar fraction of *m*-TMI in the feed is larger 16% than that of



Figure 3 Effect of *m*-TMI in feed on the (a) degree of polydispersity, (b) molecular weight of the copolymer, (c) conversion, and (d) *m*-TMI in copolymer. (60°C; AIBN, 2 wt %.) Reaction time: (\bigcirc) 6, (\square) 12, (\triangle) 18, (\bigtriangledown) 23, (\diamondsuit) 30, and (\bigcirc) 36 h.

Table IReactivity Data for *m*-TMI and STY atVarious Temperatures

Temperature (°C)	r_1	r_2	Q_2	e_2
45	1.12	0.661	0.567	-0.315
60	1.09	0.630	0.564	-0.188
75	0.949	0.543	0.557	0.013
90	0.934	0.465	0.516	0.113
AIBN = 2 wt %.				

STY: Q = 1; e = -0.8.

 r_2 , Q_2 , and e_2 are for *m*-TMI.

m-TMI in the copolymer for each reaction. These copolymers were nearly azeotropic copolymers.

Reactive Ratio and Alfrey-Price Parameter

The conversions in synthesis of the copolymers were less than 10%. The method of Fineman and Ross (1950)⁹ was used to calculate approximate values of the reactivity ratio $(r_1 \text{ and } r_2)$ by a least-squares regression that the regression factor was larger than 0.98. The uncertainties of r_1 and r_2 were within $\pm 3\%$. The nature of *m*-TMI was obtained by combining r_1 and r_2 from the copolymerization system with the Alfrey-Price equation (Alfrey et al., 1952).¹⁰ Reactivity ratios and Alfrey-Price parameters for systems according to the terminal model were calculated. The results of these calculations appear in Table I. According to the experimental data, r_1 , the reactivity ratio for STY, was larger than that for m-TMI, r_2 ; hence, the rate of consumption of STY exceeded that of *m*-TMI. These copolymerizations preferred to cross-propagate. The steric crowding and solubility of m-TMI tended to reduce the probability of incorporated another *m*-TMI molecule. The Alfrey–Price Q and e parameters are expected to be identical for m-TMI with various copolymerizations. The Q parameters (resonance) increased, and the e parameters (polarity) decreased with a temperature rise. Figure 4 displays the relationships of r_1 , r_2 , Q_2/Q_1 , and e_2 $-e_1$ versus 1/T. All straight-line plots have a good linear relationship. The effect of temperature on *r*-value is not large. The differences (e.g., E_{12} – E_{11}) of the propagation activation energies for r_1 and r_2 are 7.06 and 5.89 kJ/mol, respectively.

Thermal Analysis

Data for thermal decomposition of the copolymers in nitrogen is shown in Figures 5. The copolymer



Figure 4 Plots of (a) r_1 , (b) r_2 , Q_2/Q_1 , and $e_2 - e_1$ versus 1/T. The results are quoted from Table I.

was formed in a two-stage process. The weight loss of the first stage is due to the degradation of *m*-TMI. When the weight loss of the copolymer is equal to 5, 50, and 95%, the temperature is expressed as T_5 , T_{50} , and T_{95} , respectively. The T_5 and T_{50} for STY–*m*-TMI = 9/1 to 1/9 ranged from 325 to 195, 415 to 300, and 445 to 440, respectively. The incorporation of the STY unit into the copolymer increased its thermal stability. The T_{50} value greatly increased as the incorporated propagation of STY unit in the copolymer increased. Therefore, the incorporation of STY unit can increase the stability of the polymer backbone. The thermal stability of these copolymers was observed to be invariant with the reaction time. Figure 6 displays data for thermal decomposition of the copolymers in oxygen. The copolymer was less thermal stabile in oxygen than in nitrogen. The types of TGA curves for oxygen were different with those for nitrogen since the $T_{\rm 50}$ value decreases and $T_{\rm 95}$ value increases with an increasing mole ratio of STY-m-TMI. These copolymers indicated that the thermal stability is dependent on reaction time.

Figure 7 shows the Ozawa plots of the copolymers at various heating rates in nitrogen on various conversions of STY–m-TMI copolymer decomposition. The thermodegradation activation energy was determined by Ozawa's method¹¹ for a given value of weight fraction, as below:

$$\log \beta = -0.4567 \, \frac{E_a}{RT} + \text{constant} \tag{1}$$

where β is the heating rate, E_a is the activation energy, and R is the ideal gas constant. Thus, at the same conversion, a plot of log β versus 1/Tshould be a straight line. The activation energies were obtained as a function of conversion of copolymer decomposition, as shown in Figure 8. The degradation activation energies of these copolymers are in the range of 200 to 400 kJ/mol. Glass transition temperatures were measured with a differential scanning calorimeter; and, according to the experimental results, the range of T_g values for STY-*m*-TMI = 9/1 to 1/1 is 103 to 80°C.



Figure 5 Typical TGA scans for STY–*m*-TMI copolymers in nitrogen at 60°C and at a reaction time of (a) 12, (b) 23, and (c) 36 h. STY–*m*-TMI = (\bigcirc) 9/1, (\square) 7/1, (\triangle) 5/1, (\bigtriangledown) 3/1, (\diamond) 1/1, (\bullet) 1/3, (\blacksquare) 1/5, (\blacktriangle) 1/7, and (\bigtriangledown) 1/9.



Figure 6 Typical TGA scans for STY–*m*-TMI copolymers in oxygen at 60°C and at a reaction time of (a) 12, (b) 23, and (c) 36 h. STY–*m*-TMI = (\bigcirc) 9/1, (\square) 7/1, (\triangle) 5/1, (\bigtriangledown) 3/1, (\diamond) 1/1, (\bullet) 1/3, (\blacksquare) 1/5, (\blacktriangle) 1/7, and (\bigtriangledown) 1/9.

Viscosity and Chain Stiffness

The level of *m*-TMI in the copolymer was determined from the mass fraction of nitrogen. The experimental results of the viscometric measurements are given in Table II. A rough estimate of the experimental uncertainty in the values of $[\eta]$ is about 3%. Huggins constants were negative in the range of -2.97 to -0.96, which are smaller than values expected for linear and flexible polymers in a good solvent. The Huggins constants reported in the literature¹²⁻¹⁶ range from very low values, even negative Huggins constants, to very high ones and do not normally follow the theoretical relation ($k_{\rm H} - k_{\rm K} = 0.5$).¹⁷ The average values of ($k_{\rm H} - k_{\rm K}$), by applying the above theoretical equation, are observed to be 0.3.

The $[\eta]$ -molecular weight relationship is described by the Mark-Houwink equation:

$$[\eta] = \mathbf{K} M^{\mathbf{a}} \tag{2}$$

where both K and a are constants and dependent on the nature of the polymer, solvent, and temperature. The value of a normally ranges from 0.5 to 0.8 for a good solvent. The $[\eta]-M_w$ log-log relationship for STY-*m*-TMI = 5 copolymer was linear with a = 0.57 ± 0.03 and K = 0.4.

In order to describe chain stiffness in a quantitative manner, the characteristic ratio C_{∞} can be defined as

$$C_{\infty} = \frac{M_r K_{\theta}^{2/3}}{2l^2 \phi^{2/3}}$$
(3)

where ϕ is the Flory's constant (=250 mol⁻¹), l is the length (expressed in nanometers), and M_r is the molecular weight of the repeating unit of poly-



Figure 7 Plot of $\ln(\beta)$ as a function of thermal temperature at various conversions: (\bigcirc) 10%, (\square) 20%, (\triangle) 30%, (\bigtriangledown) 40%, and (\diamond) 50%, and STY–*m*-TMI = (a) 9/1, (b) 7/1, (c) 5/1, (d) 3/1, and (e) 1/1 for TGA curves from eq. (1).



Figure 8 Relationships between E_a (calculated from Fig. 7) and conversions of copolymer decomposition. Reaction temperatures at (a) 45, (b) 75, and (c) 90°C; and reaction time at 36 h; STY-*m*-TMI = (\bigcirc) 9/1, (\square) 7/1, (\triangle) 5/1, (\bigtriangledown) 3/1, and (\diamond) 1/1.

mer. The value of K_{θ} was obtained by using the Stockmayer–Fixman equation,¹⁸ as follows:

$$[\eta] M^{-1/2} = \mathbf{K}_{\theta} + A M^{1/2} \tag{4}$$

where A is composed of the constant ϕ and a function of polymer-solvent parameters that does not depend on molecular weight. From Figure 9, the experimental results were calculated by using experimental values of $[\eta]$ and theoretical values



Figure 9 Representation of the Stockmayer–Fixman from extrapolation to unperturbed for the STY–m-TMI = 5 copolymer. The straight line was the least-squares regression line, fitted by eq. (4).

of M_w , obtained as $M_w = ([\eta]/K)^{1/a}$ with the K and a coefficients obtained before. The straight line is the least-squares regression line, fitted by using eq. (4). The intercepts K_{θ} , calculated by the least-squares method (extrapolated to $M_w \rightarrow 0$). The intercept was 0.23 mL mol^{-0.5} g^{-1.5}. These intercepts can be converted into the characteristic ratios. The values of characteristic ratio (C_{∞}) thus obtained were 14–17. It is generally known that the value of C_{∞} calculated for polymers, assuming free rotation, is 3.2.¹⁹ Hence, the high values of C_{∞} obtained in the present study indicate a lack of rotational freedom or a high degree of stiffness for the polymer chains.

CONCLUSION

The experimental results can be summarized as follows. The a-value of the Mark–Houwink equa-

Table II Molecular Properties and Viscosity Parameters of the Copolymers in Solution

STY– <i>m</i> -TMI	<i>m</i> -TMI in Copolymer (Mol %)	$ar{M}_n imes 10^{-4}$	${ar M}_w/{ar M}_n$	$\begin{matrix} [\eta] \\ (mL \ g^{-1}) \end{matrix}$	k _H	k _K
1/1	49.0	2.58	2.84	84	-2.97	-3.13
3/1	24.6	3.52	2.86	85	-2.48	-2.97
5/1	18.5	4.03	3.60	100	-1.66	-2.89
7/1	11.4	5.54	3.30	107	-1.43	-1.68
9/1	9.13	7.19	2.83	140	-0.96	-1.31

tion was 0.57. Huggins constants were negative in the range -2.97 to -0.96 in the THF solution. The degradation activation energies of these copolymers are in the range of 200 to 400 kJ/mol. The differences of the propagation activation energies for r_1 of STY and r_2 of *m*-TMI are 7.06 and 5.89 kJ/mol, respectively. The value of the characteristic ratio thus obtained was 14–17, which indicates a lack of rotational freedom or a high degree of stiffness for the polymer chains.

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