Macromolecules **1990,** *23,* 2113-2119

Copolymerization Propagation Kinetics of Styrene with Alkyl Methacrylates

Thomas P. Davis† and Kenneth F. O'Driscoll*

Department of Chemical Engineering, University of Waterloo,
Waterloo, Ontario, Canada N2L 3E8

Mark C. Piton and Mitchell A. Winnik

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.
Received June 21, 1989; Revised Manuscript Received September 15, 1989

ABSTRACT: Copolymerizations have been carried out with styrene (STY) as monomer 1 and with ethyl (EMA), *n*-butyl (BMA), or lauryl (LMA) methacrylate as monomer 2. A pulsed UV laser was used to photoinitiate the polymerizations to low conversion. The resultant copolymers were analyzed for composition and molecular weight. Propagation rate constants were obtained as a function of composition for each of the copolymerizations, as well as reactivity ratios for the copolymerization of STY with EMA ($r_1 = 0.62$, $r_2 = 0.35$) and with BMA ($r_1 = 0.72$, $r_2 = 0.45$). None of the copolymerizations conformed to the Mayo–Lewis model with respect to their propagation rate constants. The results were interpreted using a penultimate model for propagation. Homopropagation rate constants for each of the monomers were also determined at several temperatures, allowing Arrhenius expressions to be formulated.

Introduction

The failure of the Mayo–Lewis equation to adequately describe propagation rate constants (k_p) for the copolymerization of STY with methyl methacrylate (MMA) was originally reported by Fukuda et al.[1] using the rotating sector technique. The variation of termination rate constants (k_t) with composition for this system could be interpreted either by assuming a cross-termination constant (ϕ) of 1 or by adopting the simple equation suggested by North and co-workers[2,3] where the copolymerization termination rate constants were given as weighted averages of the homotermination rate constants. Davis et al.[4] subsequently verified this finding using an alternative experimental technique where a pulsed laser was used as an initiation source for radicals, and gel-permeation chromatography (GPC) was used to analyze the products. This technique has the advantage of measuring k_p independently of k_t. As Fukuda et al.[1] established that termination could be described by a weighted average procedure O'Driscoll and Huang[5] utilized copolymerization rate data to calculate the variation of k_p with feed composition for the STY/MMA copolymerization and obtained similar results to those reported by Davis et al.[4] A penultimate model to describe the experimental data was proposed by Fukuda et al.[6]

$$k_p = \frac{\bar{r}_1 f_1^2 + 2 f_1 f_2 + \bar{r}_2 f_2^2}{[\bar{r}_1 f_1/\bar{k}_{11}] + [\bar{r}_2 f_2/\bar{k}_{22}]} \tag{1}$$

$$\bar{r}_1 = \frac{r_1'[f_1 r_1 + f_2]}{f_1 r_1' + f_2} \qquad \bar{r}_2 = \frac{r_2'[f_2 r_2 + f_1]}{f_2 r_2' + f_1} \tag{2}$$

$$\bar{k}_{11} = \frac{k_{111}[r_1 f_1 + f_2]}{r_1 f_1 + [f_2/s_1]} \qquad \bar{k}_{22} = \frac{k_{222}[r_2 f_2 + f_1]}{r_2 f_2 + [f_1/s_2]} \tag{3}$$

where f_i = mole fraction of monomer i in the feed, $r_i = k_{iii}/k_{iij}$, $r_i' = k_{jii}/k_{jij}$, and $s_i = k_{jii}/k_{iii}$. These rate constants refer to the following kinetic scheme for propagation:

$$\text{-}M_iM_j^{\bullet} + M_k \xrightarrow[i,j,k\,=\,1\text{ or }2]{k_{ijk}} M_iM_jM_k^{\bullet}$$

Since composition measurements for STY–MMA do conform to the standard Mayo–Lewis scheme, then r_i must equal r_i'. The penultimate influence is asserted through the parameters s_1 and s_2, which do not influence composition or sequence distribution.[7] A chemical basis for this model was outlined by Fukuda et al.,[6] where radical stabilization energies were assumed to vary according to the nature of the penultimate unit. That penultimate effects occur cannot be regarded as surprising, as recent work by several authors using either low molecular weight model compounds[8] or ESR[9] has shown the presence of penultimate effects.

Previously, these copolymerization rate "abnormalities" were attributed to the termination reaction and analyzed in terms of a cross-termination constant, ϕ, which can be defined as

$$\phi = \frac{k_{t12}}{2[k_{t11}k_{t22}]^{1/2}} \tag{4}$$

where k_{tii} refers to the homotermination rate constants and k_{12} to the cross-termination reaction. This approach assumes that the termination reaction in polymerization is chemically controlled. Overwhelming experimental evidence now indicates that it is diffusion controlled.

An improved scheme accounting for diffusion control in termination was proposed by Russo and co-workers[10] but was found to be deficient.[11] Several previous papers[12,13] reported on the copolymerizations of STY with alkyl methacrylates. The results were interpreted on the basis of termination kinetics, with the assumption that ultimate kinetics prevail in the propagation reaction.

The intention of this paper is to describe experimental results obtained using the pulsed laser technique, for the copolymerization of STY with EMA, BMA, and LMA. These experiments were performed to investigate the nature of the propagation reactions in these systems. STY

---

* To whom correspondence should be addressed.

† Present address: ICI Chemicals & Polymers Ltd., Research & Technology, P.O. Box 8, The Heath, Runcorn, Cheshire, U.K. WA7 4QD.

0024-9297/90/2223-2113$02.50/0

Table I
Effect of Temperature on Propagation Rate Constants ($L\ mol^{-1}\ s^{-1}$) for the Homopolymerizations of STY, EMA, BMA, and LMA

T, K	STY	EMA	BMA	LMA
283				300
293				386
298	78[a]	258	274	
303				452
308	120	356	392	
313				601
318	168	424	502	
323				796
328	249	589	656	

[a] Data from ref 14.

is denoted as M_1 throughout this paper and the alkyl methacrylates are denoted as M_2.

Experimental Section

Materials. All monomers were washed with aqueous sodium hydroxide, dried over calcium hydride, and distilled under an atmosphere of nitrogen at reduced pressure. The initiators 2,2′-azobis(isobutyronitrile) (AIBN) and benzoin (BZ) were recrystallized three times from methanol and ethanol, respectively. Toluene was distilled prior to use. Tetrahydrofuran (THF) for GPC measurements was used directly from the manufacturer (Caledon).

Polymerizations. The relevant freshly distilled monomers (total volume 2–4 mL) and initiator (5×10^{-3} M) were charged to Pyrex ampules (square cells 1 cm × 1 cm) and subsequently degassed and sealed. The reaction mixture was kept frozen in liquid nitrogen until required. Full details of the experimental setup are given in preceding publications.[4,14] A pulsed UV laser generates light of 355 nm at a pulsing rate of 0.1–10 Hz. The beam is directed through the base of the cell to minimize unexposed volume. Conversions <4% were obtained. Samples for NMR analysis were precipitated in methanol, isolated, and dried in vacuo at 313 K.

Analysis. NMR. ^1H FT-NMR spectra were recorded at room temperature on a 250-MHz Bruker instrument. Samples were dissolved in carbon tetrachloride. Copolymer compositions were obtained from peak area differences between the aromatic and aliphatic regions of the spectra.

GPC. The samples were analyzed on a Waters GPC-590 fitted with three μStyragel columns (10^5, 10^3, 10^2 Å) using THF as eluant at 298 K. Calibration was conducted using P(STY) standards of narrow polydispersity. The molecular weight of the alkyl methacrylate homopolymers was obtained via the universal calibration using known Mark–Houwink constants.[15,16] The molecular weight of the copolymer samples was obtained by a weighted average procedure as described previously.[4] As the results reported in this paper are critically dependent on the calibration, all the tabulated data and the GPC calibration polynomials are available as supplementary material.

Results and Discussion

Homopolymerizations. Polymerizations were conducted at temperatures in the range 283–328 K for each of the monomers. From the molecular weight distributions the chain length (υ) generated between successive laser pulses was obtained. As previously we take υ to be the inflection point on the low molecular weight side of the molecular weight distribution. The propagation rate constant can be calculated from the simple interrelation given as eq 5[17] where [M] is the monomer concentration and t_f is the dark time between successive laser flashes.

$$\upsilon = k_p[M]t_f \qquad (5)$$

The results are shown in Table I. Using these data, Arrhenius plots were constructed, which are depicted in Figure 1. The following expressions were formulated (RT in kilojoules per mole):

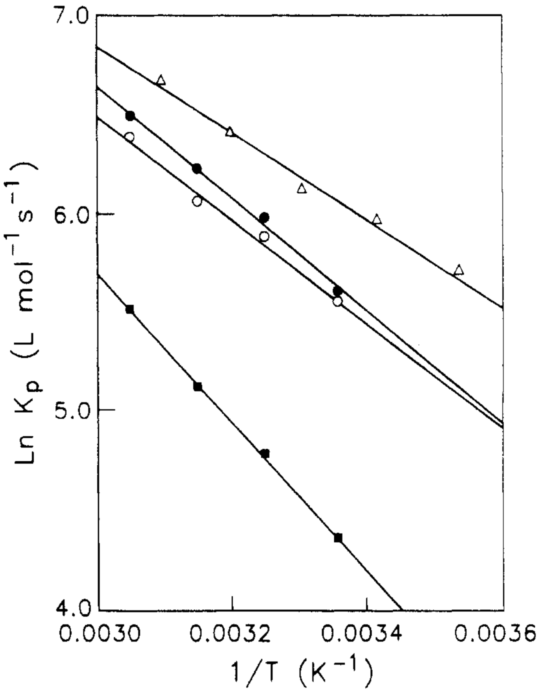

Figure 1. Plots of ln k_p vs $1/T$ for STY (■), EMA (○), BMA (●), and LMA (△).

$$\text{STY} \qquad k_p = 1.99 \times 10^7 \exp\{-30.78/RT\} \qquad (6)$$

$$\text{EMA} \qquad k_p = 1.50 \times 10^6 \exp\{-20.46/RT\} \qquad (7)$$

$$\text{BMA} \qquad k_p = 3.44 \times 10^6 \exp\{-23.3/RT\} \qquad (8)$$

$$\text{LMA} \qquad k_p = 2.93 \times 10^5 \exp\{-16.19/RT\} \qquad (9)$$

The Arrhenius expression for MMA was reported earlier using the SIP reactor.[19] Homopolymerizations done using the laser technique at two temperatures (298 and 313 K) were found to be in accord with this expression, which is given below for comparison purposes:

$$\text{MMA}^{19} \qquad k_p = 4.92 \times 10^5 \exp\{-18.10/RT\} \qquad (10)$$

All of the homopolymerizations were performed in bulk except for the LMA, where initial experiments indicated that the primary GPC peak required for analysis was not clearly delineated for this system. The molecular weight distribution profile is dependent not only on the propagation reaction but also on the termination reaction. In the LMA homopolymerization the termination rate constant is some 30 times lower than that for MMA polymerization.[18] As a consequence the rate of termination in a non-steady-state experiment is also slower by the same degree. The primary factor causing the low k_t is the viscosity of the monomer.[18] Therefore, the samples were diluted by 50% using toluene. Typical GPC traces are shown in Figure 2; these may be compared with GPC chromatograms reported earlier for MMA polymerization.[14]

The result for STY is in excellent agreement with that reported by Mahabadi and O'Driscoll[19] using the SIP reactor, which has been set as a benchmark by an IUPAC Working Party.[20] Previous authors[21,22] have found that the propagation reaction in alkyl methacrylates is relatively unaffected by the size of the alkyl group. The results reported here for EMA and BMA are in accord with this finding. However, the result for LMA indicates a lower

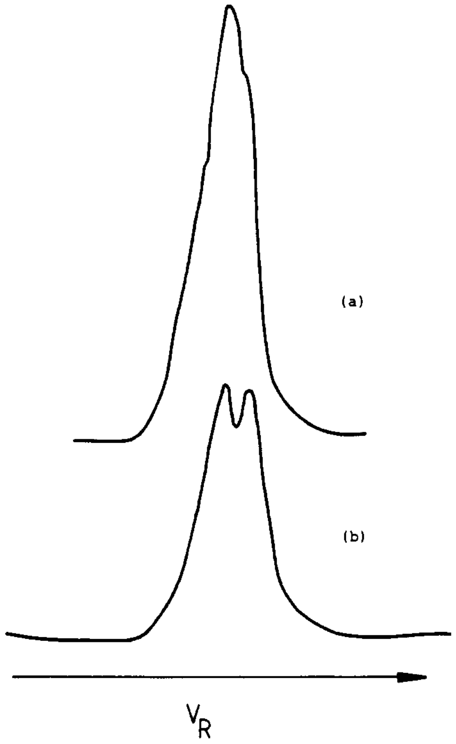

Figure 2. GPC chromatograms of poly(LMA), V_R = retention volume: (a) bulk polymerization, t_f = 0.4 s, T = 328 K; (b) solution polymerization (50% v/v toluene), t_f = 0.2 s, T = 323 K.

Table II
Effect of Temperature on Rate Parameters for EMA Polymerization

	T, K			
rate param	363	353	343	333
$k_t/k_p{}^2$,[a] mol s L^{-1}	9.1	12.4	17.7	24.01
$k_p(fk_d/k_t)^{0.5}$,[a] $(L/mol)^{0.5}$ s^{-1}	4.2×10^{-3}	1.9×10^{-3}	8.9×10^{-4}	3.8×10^{-4}
$k_t \times 10^{-6}$, L mol^{-1} s^{-1}	11.97	11.10	10.55	9.29
$fk_d \times 10^5$, s^{-1}	16.0	4.48	1.4	0.347

[a] Data of Cardenas.[23]

activation energy and consequently a larger k_p value at any set temperature. Of course the values obtained using the pulsed laser technique rely heavily on the GPC calibration and hence on the Mark–Houwink constants in this case.[16]

The k_p data reported here for EMA can be combined with earlier rate measurements reported by Cardenas[23] to give k_t and fk_d data (for AIBN initiation) at different temperatures as shown in Table II. The relevant Arrhenius expressions are given as eqs 11 and 12.

$$k_t = 1.76 \times 10^8 \exp\{-8.09/RT\} \tag{11}$$

$$fk_d = 0.252 \exp\{-5.63/RT\} \tag{12}$$

Copolymerizations. Reactivity ratios for the copolymerizations (at 328 K) of STY with EMA and BMA were determined using nonlinear regression, the relevant data are given in Table III. Experimental design was primarily oriented to propagation studies so Tidwell–Mortimer[24] criteria were not adhered to. The point estimates were r_{STY} = 0.62, r_{EMA} = 0.35 and r_{STY} = 0.72, r_{BMA} = 0.45. The 95% confidence regions are depicted in Figures 3 and 4 Very low conversions for the STY/LMA copolymerization confounded attempts at copolymer isolation so values were taken from literature.[25] These estimates are given as r_{STY} = 0.57, r_{LMA} = 0.45. For this work we have assumed that the reactivity ratios r_1 and r_2 are unaffected by temperature. As reported by Odian,[28] an examination of various compilations of r_1 and r_2 shows that they are relatively insensitive to temperature provided that propagation is irreversible.

Table III
Composition Data for the Low Conversion Copolymerization of STY (M_1) with EMA and BMA[a]

STY/EMA		STY/BMA	
f_1	F_1	f_1	F_1
0.821	0.768	0.907	0.890
0.821	0.771	0.907[b]	0.907
0.821[b]	0.803	0.907	0.883
0.527	0.584	0.907	0.882
0.255	0.374	0.720	0.711
0.255	0.372	0.720	0.704
0.255	0.349	0.454	0.514
0.255	0.362	0.454	0.504
0.067	0.133	0.454	0.521
0.067	0.125	0.454	0.518
		0.126	0.198
		0.126	0.202

[a] f_1 = mole fraction of styrene in the feed. F_1 = mole fraction of styrene in the copolymer. [b] If these data points are excluded, the confidence intervals are considerably reduced. However, there is no obvious reason for their omission, and they have been retained.

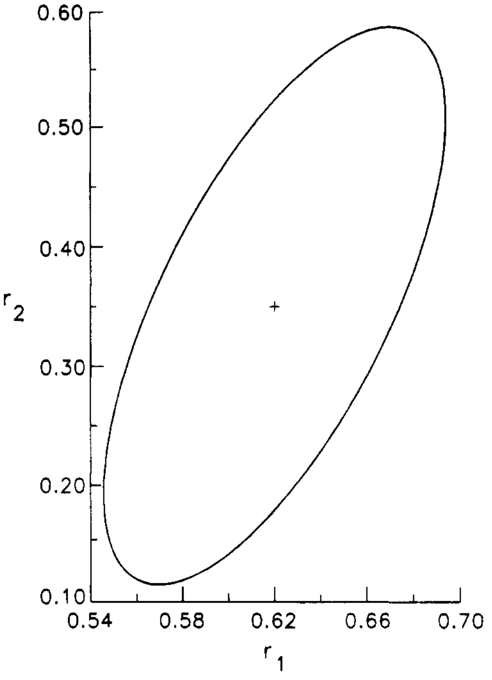

Figure 3. 95% confidence region for the STY/EMA reactivity ratios; estimate obtained using nonlinear regression.

The STY/EMA and STY/BMA copolymerizations were done in bulk; the STY/LMA was copolymerized in solution (toluene) for reasons already discussed. All three copolymerizations were carried out at 298 K. In addition, the copolymerizations of STY with EMA and BMA were performed at 328 K. Plots of k_p vs f_1 for all these copolymerizations are shown in Figures 5–9. *It is evident that none of the copolymerization propagation rate constants can be described by the Mayo-Lewis model.* Consequently, the data have been fitted to Fukuda's model.[6] The r_1, r_2, s_1, s_2, r_1r_2, and s_1s_2 values are given in Table IV. 95% confidence intervals for the s_1 and s_2 values from the copolymerization of STY with EMA at two different temperatures are given in Figure 10. Likewise, those for the STY/BMA copolymerization are shown

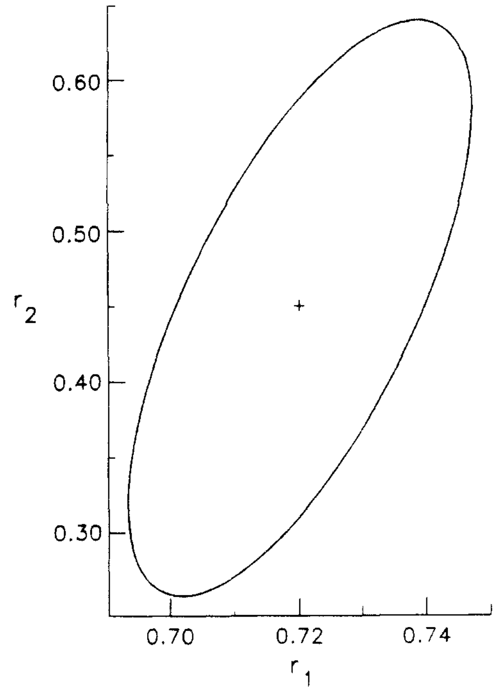

Figure 4. 95% confidence region for the STY/BMA reactivity ratios; estimate obtained using nonlinear regression.

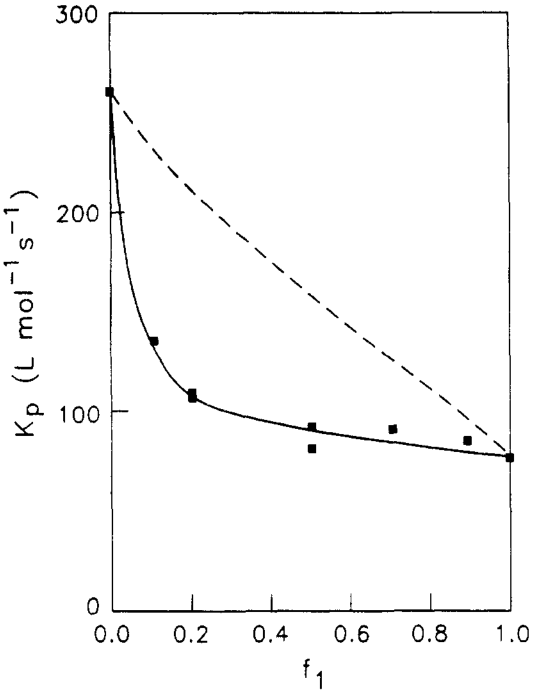

Figure 5. Plot of k_p vs f_1 for the copolymerization of STY with EMA at 298 K. The dashed and solid lines represent the Mayo-Lewis and penultimate model predictions, respectively.

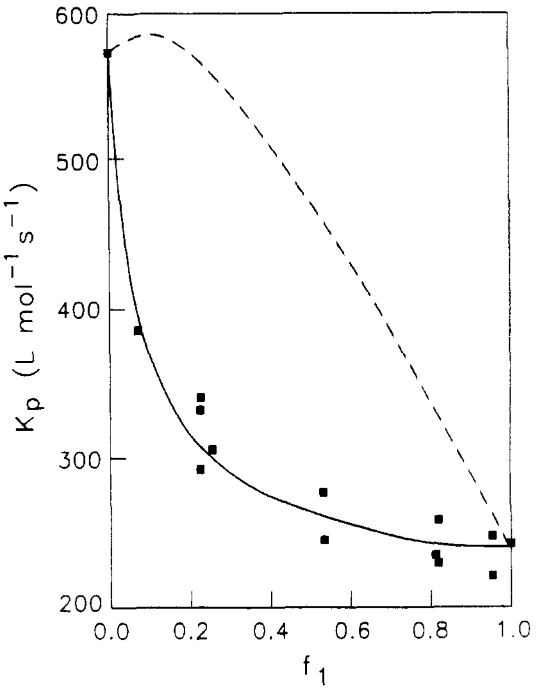

Figure 6. Plot of k_p vs f_1 for the copolymerization of STY with EMA at 328 K. The dashed and solid lines represent the Mayo-Lewis and penultimate model predictions, respectively.

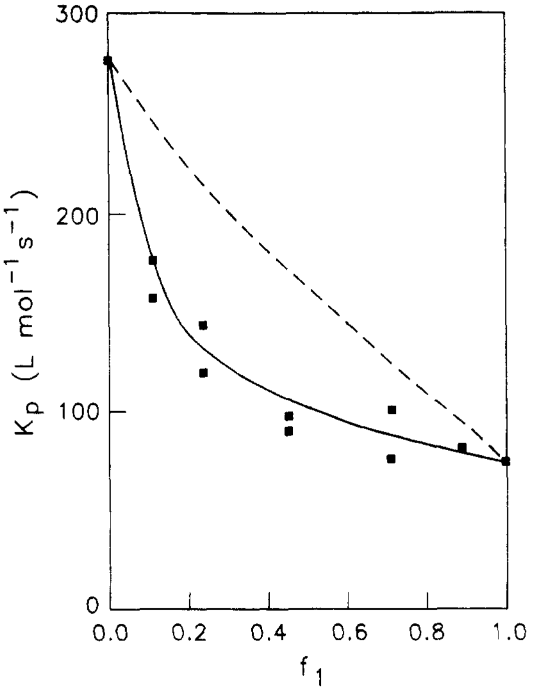

Figure 7. Plot of k_p vs f_1 for the copolymerization of STY with BMA at 298 K. The dashed and solid lines represent the Mayo-Lewis and penultimate model predictions, respectively.

in Figure 11. The first point to note is the increased uncertainty of the results compared to those reported for the STY/MMA copolymerization.[4] This is probably a consequence of extra error introduced by using the universal calibration for GPC. Because of this increased uncertainty, no definitive statement can be made regarding the effect of temperature on s_1 and s_2. It has been noted previously, however, that the effect of temperature on the ϕ factor is minimal.[26] It would appear then that the ϕ factor is only of use as an adjustable parameter to fit copolymerization rate data and has no physical meaning. However, the magnitude of ϕ and the extent to which it varies for a particular copolymerization can be seen as a guide to the deviation of propagation kinetics from the Mayo-Lewis model. In this respect it is interesting to note that the ϕ factor has been correlated with r_1r_2 in several publications,[27,28] both tending to unity in a concomitant fashion. The Fukuda model also predicts decreasing penultimate effects in the same way. The confidence interval for s_1 and s_2 from the STY/LMA copolymerization has been plotted along with all the confidence intervals obtained at 298 K (including that for the STY/MMA copolymerization[4]) for comparison purposes in Figure 12. The striking feature is the very large confidence interval obtained for STY/BMA. All that can

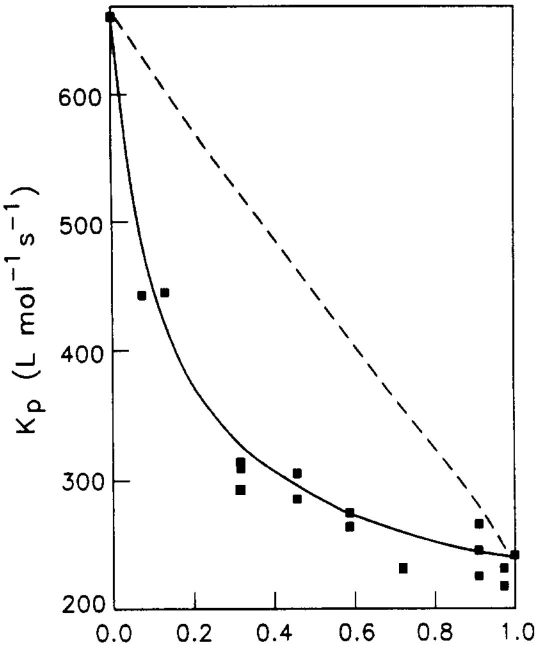

Figure 8. Plot of k_p vs f_1 for the copolymerization of STY with BMA at 328 K. The dashed and solid lines represent the Mayo-Lewis and penultimate model predictions, respectively.

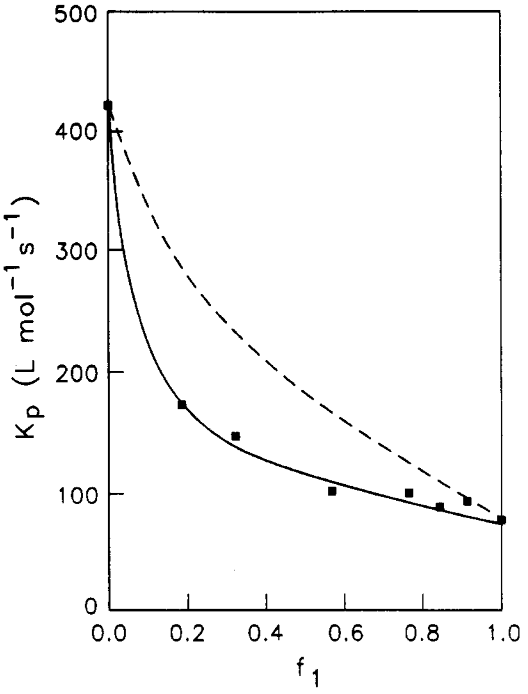

Figure 9. Plot of k_p vs f_1 for the copolymerization of STY with LMA at 298 K. The dashed and solid lines represent the Mayo-Lewis and penultimate model predictions, respectively.

Table IV
Reactivity Ratios for the Copolymerization of STY (M_1) with EMA, BMA, and LMA (M_2)

M_2	T, K	r_1	r_2	s_1	s_2	r_1r_2	s_1s_2
EMA	298	0.62	0.35	0.62	0.21	0.22	0.13
EMA	328	0.62	0.35	0.46	0.45	0.22	0.21
BMA	298	0.72	0.45	0.56	0.63	0.32	0.35
BMA	328	0.72	0.45	0.50	0.67	0.32	0.34
LMA	298	0.57	0.45	0.59	0.33	0.26	0.19

be noted with confidence is that the three copolymerizations reported here do result in significantly different s_i values when compared to those of the STY/MMA system. However, no similar legitimate statement can be made regarding significant differences among the s_i values for the copolymerizations of STY with EMA, BMA, and LMA.

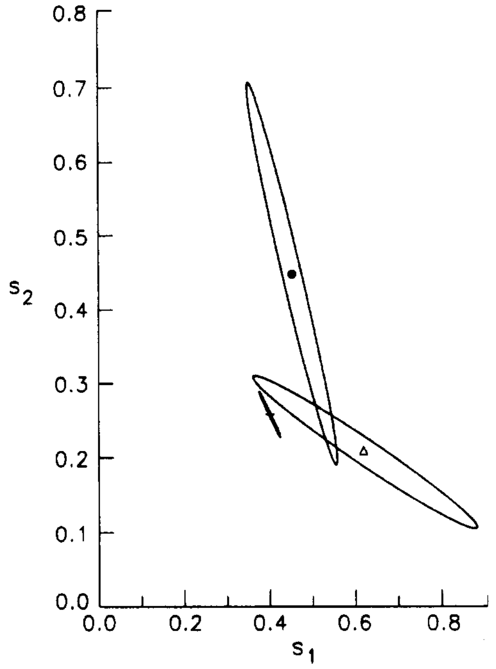

Figure 10. 95% confidence regions for s_1 and s_2 from the pulsed laser copolymerization of STY with EMA, at two different temperatures: 298 K (△) and 328 K (●). In addition the 95% confidence region for s_1 and s_2 is plotted for the rate data (at 333 K) of Chaudhari and Palit[13] (+).

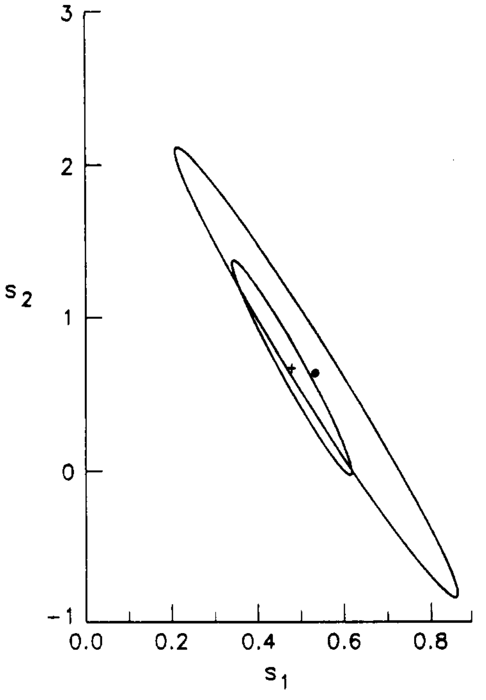

Figure 11. 95% confidence regions for s_1 and s_2 from the pulsed laser copolymerization of STY with BMA, at two different temperatures: 298 K (●) and 328 K (+).

The confidence intervals given here can be compared with the very large confidence interval[4] that was calculated for the STY/MMA data of Fukuda et al.[1], obtained using the rotating sector technique. Therefore the pulsed laser procedure still appears to compare very favorably with the main alternative method for derivation of individual rate constants.

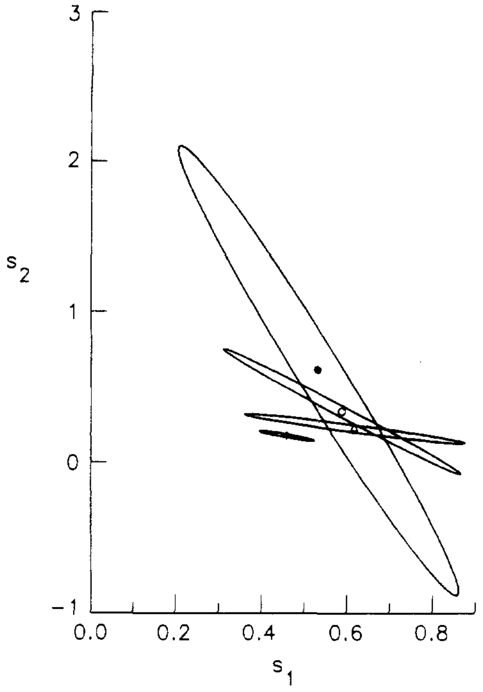

Figure 12. 95% confidence regions for s_1 and s_2 from the pulsed laser copolymerization at 298 K of STY with MMA (+), EMA (△), BMA (●), and LMA (○).

An alternative approach to obtaining s_i values was used by O'Driscoll and Huang[5] as described earlier. Having established that k_t in copolymerization can be described by a simple weighted average of homotermination rate constants, it is possible to derive s_i values from standard rate (R_p) measurements. O'Driscoll and Huang[5] achieved very tight confidence intervals for their data on STY/MMA, which suggests that this method may be suitable for good point estimation (provided the experiment is designed to produce high polymer above the molecular weight range where chain length effects are important in termination). We have reanalyzed the rate data of Chaudhuri and Palit[13] for STY/EMA at 333 K, which fulfills the above criteria. EMA homopolymerization rate constants for AIBN initiation and termination were taken from eqs 11 and 12, together with the homotermination rate constant for STY.[19] Variation of termination and initiation rate constants with composition were simply taken as weighted averages of the homopolymerization rate constants, and k_p was computed as a function of monomer feed (f_1). All the data are plotted in Figure 13. The derived k_p values were fitted to Fukuda's model using nonlinear regression, and point estimates for s_1 and s_2 were calculated to be 0.43 and 0.23, respectively, with a very narrow confidence interval shown in Figure 10 to allow comparison with the confidence intervals obtained for the same copolymerization using the pulsed laser technique.

Conclusions

The results reported clearly show that the Mayo–Lewis model fails to predict propagation rate constants for the copolymerization of STY with EMA, BMA, or LMA. The results can be fitted to Fukuda's penultimate model. The extreme sensitivity of the pulsed laser technique to the GPC calibration (as reported earlier[14]) results in large uncertainties in s_1 and s_2. This fact is probably a consequence of errors introduced by adoption of a universal calibration for the GPC determination of molecular weight.

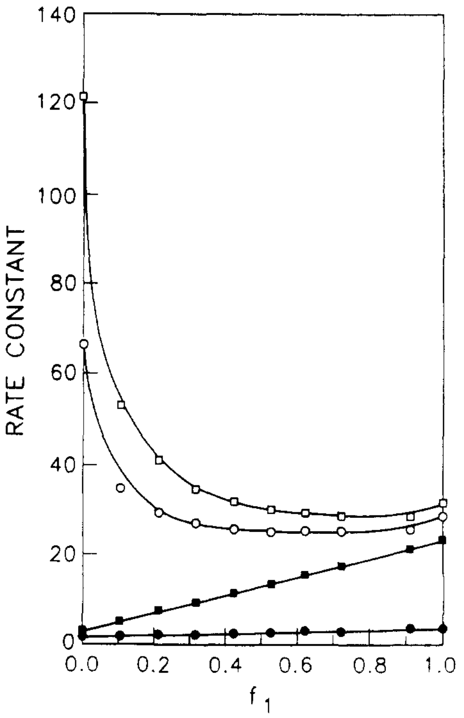

Figure 13. Plot of rate constant vs f_1 for STY/EMA copolymerization rate data at 333 K.[13] The ordinate scale has the following multipliers for convenience: $fk_d[I]$ (●), 10^8; k_t (■), 3×10^{-7}; k_p (○), 10^{-1}; R_p (□), 5×10^5.

Recent work by Ito[29] on the copolymerization of acrylonitrile and MMA using ferric chloride as terminator suggests that there is no deviation from Mayo–Lewis kinetics in this system, and he therefore concludes that any "abnormal" effects originate in the termination reaction. However, studies using the pulsed laser technique verify Fukuda's original result for MMA–STY[4] and now for STY with EMA, BMA, and LMA. This procedure allows for calculation of k_p independent of any abnormal effects in the termination reaction. Bamford[30] has recently described the consequences of adopting the penultimate model explanation prefered by Fukuda et al.[6] with regard to "moderated" copolymerizations either in the presence of a chain-transfer agent or a retarder (such as ferric chloride). If the experimental data are accepted, then for the copolymerization of STY with MMA in the presence of 1-butanethiol, the following relations are imposed

$$\lambda_{11s}/\lambda_{21s} = k_{112}/k_{212} = k_{111}/k_{211}$$

$$\lambda_{12s}/\lambda_{22s} = k_{121}/k_{221} = k_{122}/k_{222}$$

where the propagation and transfer coefficients are denoted by k and λ, respectively. The subscript s refers to the chain-transfer agent.

In conclusion, experimental evidence obtained from copolymerizations performed in the absence of any additive e.g., chain-transfer agent or retarder) does indicate that any abnormal effects in copolymerization kinetics are related to propagation and not the termination reaction.

Acknowledgment. Support of this work by the Natural Sciences and Engineering Research Council of Canada is greatly appreciated.

Supplementary Material Available: Tables of data for copolymerizations of STY with EMA at 298 and 328 K, of STY with BMA at 298 and 328 K, and of STY with LMA at 298 K

Macromolecules 1990, *23*, 2119–2124 2119

and of GPC calibration polynomials (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Fukuda, T.; Ma, Y.-D.; Inagaki, H. *Macromolecules* **1985**, *18*, 17.

(2) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.

(3) Atherton, J. N.; North, A. M. *Trans. Faraday Soc.* **1962**, *58*, 2049.

(4) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 181.

(5) O'Driscoll, K. F.; Huang, J. *Eur. Polym. J.* **1989**, *25*, 629.

(6) Fukuda, T.; Ma, Y.-D.; Inagaki, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 495.

(7) O'Driscoll, K. F.; Davis, T. P. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 417.

(8) Prementine, G. S.; Tirrell, D. A. *Macromolecules* **1989**, *22*, 52.

(9) Tanaka, H.; Sasai, K.; Sato, T.; Ota, T. *Macromolecules* **1988**, *21*, 3536.

(10) Bonta, G.; Gallo, B. M.; Russo, S. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1727.

(11) Ito, K.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3913.

(12) Ito, K. *J. Polym. Sci, Part A-1* **1971**, *9*, 867.

(13) Chaudhuri, A. K.; Palit, S. R. *Makromol. Chem.* **1969**, *121*, 33.

(14) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.

(15) Samay, G. *Acta Chim. Acad. Sci. Hung.* **1979**, *102*, 157.

(16) Mahabadi, H. K.; O'Driscoll, K. F. *J. Appl. Polym. Sci.* **1977**, *21*, 1283.

(17) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(18) Mahabadi, H. K.; O'Driscoll, K. F. *J. Polym. Sci., Part C: Polym. Lett.* **1976**, *14*, 671.

(19) Mahabadi, H. K.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1977**, *A11*, 967.

(20) Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 293.

(21) Yokota, K.; Kani, M.; Ishii, Y. *J. Polym. Sci., Part A-1* **1968**, *6*, 1325.

(22) Plate, N. A.; Ponomarenko, A. G. *Polym. Sci. USSR* **1974**, *16*, 3067.

(23) Cardenas, J. N. Ph.D. Thesis, University of Waterloo, 1976.

(24) Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci.: Part A* **1965**, *3*, 369.

(25) Otsu, T.; Ito, T.; Imoto, M. *J. Polym. Sci., Part B* **1965**, *3*, 113.

(26) Bonsall, E. P.; Valentine, L.; Melville, H. W. *J. Polym. Sci.* **1951**, *7*, 39.

(27) Rudin, A.; Chiang, S. S. M. *J. Macromol. Sci., Chem.* **1974**, *9*, 237.

(28) Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981.

(29) Ito, K. *Polym. Commun.* **1988**, *29*, 223.

(30) Bamford, C. H. *Polym. Commun.* **1989**, *30*, 30.

Registry No. STY, 100-42-5; EMA, 97-63-2; BMA, 97-88-1; LMA, 142-90-5.

Synthesis and Characterization of a Water-Soluble Poly(*p*-phenylenevinylene) Derivative

Songqing Shi and Fred Wudl*

Institute for Polymers and Organic Solids, Department of Physics and Department of Chemistry, University of California, Santa Barbara, California 93106.

Received August 1, 1989; Revised Manuscript Received October 24, 1989

ABSTRACT: We report the preparation of a water-soluble poly(*p*-phenylenevinylene) (PPV) derivative, poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene], by a conventional precursor polymer approach. The conversion of the precursor polymer into fully conjugated PPV can be carried out in solution and in the solid state. We also describe a novel way to hydrolyze a sulfonyl chloride in the precursor polymer by refluxing with a small amount of DMF in water. Electronic spectroscopy reveals that the as-formed polymer is Brønsted acid doped and that it can be compensated (undoped) with ammonia.

Introduction

Highly conjugated polymers are generally insoluble, infusible, and intractable because of the stiffness of their backbones. The intractability makes it difficult to process electrically conductive polymers into useful objects such as fibers and films. One of the methods developed to solve this problem is the use of a processible precursor polymer that can be converted to the desired conjugated polymer without loss of the degree of polymerization and physical shape. Edwards and Feast's polyacetylene was synthesized by this approach.[1]

Highly conducting poly(*p*-phenylenevinylene) (PPV) has been obtained via pyrolysis of the soluble precursor polymer derived from *p*-xylene-α,α'-bis(dimethylsulfonium bromide) under an inert atmosphere.[2] Contrary to common observations that introduction of a substituent group to conjugated polymers results in a decrease in electric conductivity, unstretched, alkoxy-substituted PPV showed considerably higher conductivity than the corresponding, unstretched, PPV.[3] More recently, the first organic solvent soluble derivative of PPV, the dihexyloxy-substituted PPV, was developed through a novel route, where the precursor polymer was converted into a fully conjugated polymer in an organic solvent instead of in the solid state.[4]

The first water-soluble conducting polymers are poly(3-thiophenealkanesulfonates) invented in our group.[5] In these polymers, the counterions are covalently bound to the polymer backbone, leading to the self-doping concept.

In this paper we present the results on the first water-soluble PPV derivative.[6] This was achieved by the introduction of an alkanesulfonate group to the monomer. Such a modification not only did make the resulting PPV easily water soluble and self-doped but also lowered its band gap as in the case of alkoxy substitution of PPV.

0024-9297/90/2223-2119$02.50/0