Polymer 42 (2001) 495–500

polymer

www.elsevier.nl/locate/polymer

An assessment of the copolymerization reaction between styrene and 2-methylene-1,3-dioxepane

L.M. Morris, T.P. Davis*, R.P. Chaplin

School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney 2052, Australia

Received 24 January 2000; received in revised form 30 March 2000; accepted 20 April 2000

Abstract

The copolymerization behaviour of 2-methylene-1,3-dioxepane (MDO) with styrene has been studied via pulsed-laser polymerization. The average propagation rate coefficients, $\langle k_p \rangle$,were determined for a number of feed ratios of MDO ranging from 0 to 0.938 at both 30 and 40°C. Both the $\langle k_p \rangle$ and the polymer composition data indicate a complete absence of copolymerization — contrary to a previously published study. The experimental data indicate the homopolymerization of styrene, with the MDO merely acting as a diluent. © 2000 Published by Elsevier Science Ltd.

Keywords: 2-Methylene-1,3-dioxepane; Styrene; Copolymerization

1. Introduction

Free radical ring-opening polymerizations have been studied by a number of different research groups over the past 40 years. However, many of the previous studies have concentrated on the synthetic aspects of the polymerization and little reliable kinetic and mechanistic data exist for this class of reaction. One well-known ring-opening monomer is the cyclic ketene acetal, 2-methylene-1,3-dioxepane (MDO). This monomer has been shown to undergo 100% ring opening at 25°C to yield polycaprolactone via the mechanism shown in Fig. 1 [2–7]. A recent investigation into the copolymerization of MDO with methyl methacrylate (MMA) using pulsed-laser polymerization (PLP) noted an unusual kinetic behaviour, with the results proving inconsistent with the common copolymerization models [11]. More recently, in situ NMR studies of the polymerization of MDO at 65°C, have provided strong evidence that the chain carrier in the ring-opening polymerization of MDO is indeed a free radical. The precise nature of the ring-opening mechanism in MDO has been the subject of conjecture for a number of years since Bailey suggested that the polymerization of MDO may take place via a concerted intermediate [3]. However, the weight of extant evidence is in favour of radical intermediates, as shown by a number of different studies such as the polymerization of an optically active cyclic ketene acetal [1], which demonstrated a lack of stereoregularity and the observation that the radical-backbiting plays a role in MDO polymerization yielding a highly branched polymer structure [9].

The only previous study on the kinetics of the copolymerization of MDO with styrene (STY) was limited to the measurement of reactivity ratios [4] by Bailey et al. who reported values for the reactivity ratios, r_{MDO} and r_{STY} as 0.021 and 22.6, respectively. The value for r_{STY} seems low when compared to the reactivity ratios of MDO with MMA where r_{MDO} and r_{MMA} were reported as 0.06 and 34, respectively [11]. However, it is clear that MDO has a low propensity to copolymerize with many common monomers. The purpose of the work reported herein is to assess the copolymerization behaviour of MDO with STY in order to clarify some of the current contradictions and unexplained behaviour previously reported in the literature.

2. Experimental

2.1. Synthesis of 2-methylene-1,3-dioxepane

The preparation of MDO has been reported previously [10].

2.2. Pulsed-laser polymerizations

Comonomer mixtures at various feed ratios of MDO and STY (total mass ~1 g) together with benzoin were prepared

---

* Corresponding author. Tel.: +61-2-9385-4371; fax: +61-2-9385-6250.
E-mail address: t.davis@unsw.edu.au (T.P. Davis).

PII: S0032-3861(00)00336-0

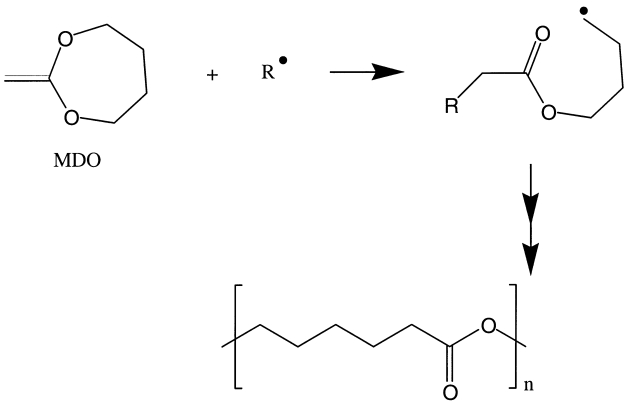

Fig. 1. Polymerization of 2-methylene-1,3-dioxepane (MDO).

in 3 ml pyrex vessels. The solutions were degassed by purging with nitrogen and then sealed. Polymerizations were carried out in a Nd–YAG laser beam at 355 nm at pulse frequencies ranging from 1 to 4 Hz. The polymerizations were stopped by precipitating the samples into methanol. The resulting polymer was allowed to settle, and the excess methanol was decanted off. The samples were then dried to constant mass under vacuum at 40°C. Polymerizations were performed in bulk at 30 and 40°C and at 50% dilution with toluene at 40°C.

2.3. Measurement of copolymer compositions

Copolymer compositions were measured via ^{1}H-NMR using a Bruker 300 MHz NMR. The mole fraction of styrene in the copolymer was determined by asssuming that the aromatic peaks in the spectra originate solely from styrene groups within the chain. Consequently, the mole fraction of styrene in the copolymer is estimated from $8/5\times$ the aromatic signal, divided by the sum of all the integrals in the spectra.

2.4. Gel permeation chromatographic analysis

Molecular weight distributions were obtained by gel permeation chromatography (GPC) using a Shimadzu LC-10AT Liquid Chromatograph pump, a Shimadzu SIL-10A Autoinjector, a column set consisting of a Polymer Laboratories (PL) 3.0 μm bead-size guard column (50×7.5 mm) followed by three linear PL columns (10^5, 10^4 and 10^3) (300×7.5 mm) and a Shimadzu RID-10A Refractive Index Detector. Tetrahydrofuran (BDH, HPLC grade) was used as the eluent at 1 ml/min. Calibration of the GPC equipment was effected with narrow poly(methyl methacrylate) and polystyrene standards (Polymer Laboratories, molecular weight range: $200–6.886\times10^5$). Quantitative molecular weight analyses were performed assuming a polystyrene calibration curve. These assumptions proved

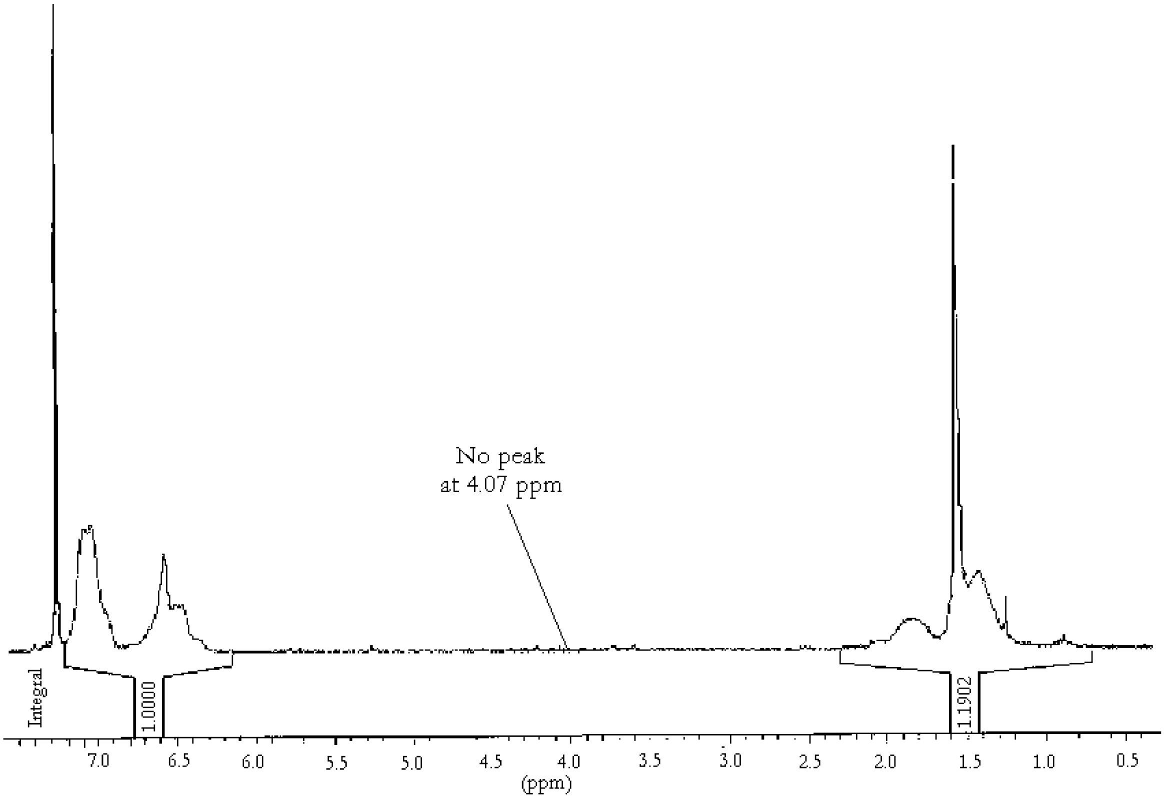

Fig. 2. ^{1}H-NMR spectra for the copolymerization of MDO and STY at 30°C and $f_{\mathrm{MDO}} = 0.607$. Note the absence of any peak at 4.07 ppm corresponding to the methylene protons adjacent to the ester group in poly-MDO.

Table 1
Polymerization conditions, molecular weights and propagation rate constants at 30°C

f_{MDO}	Initiator concentration $[I]$ ($\times 10^{-2}$ mol l^{-1})	Frequency (Hz)	Reaction time (min)	Primary inflection molecular weight (log M_{inf1})[c]	Overtone inflection weight (log M_{inf2})	$\langle k_p \rangle$ (l mol^{-1} s^{-1})
0.0000	0.995	2	40	4.6945	5.0025	110
0.0000	0.846	4	20	4.3901	4.6949	109
0.1075	2.74	4	26	4.3525	4.6447	100
0.1209	2.12	2	52	4.6417	4.9376	97
0.2362	2.66	4	27	4.2896	4.5936	86
0.2144	2.12	2	50	4.5886	4.8937	86
0.4331	2.86	4	30	4.1579	4.4673	63
0.4353	1.86	2	60	4.4521	4.7548	62
0.6070	2.64	4	30	4.0058	4.3084	44
0.6111	2.84	2	60	4.2952	4.5999	43
0.8088	2.49	4	40	3.6991	3.9999	22
0.8016	2.90	2	85	4.0067	4.3178	22
0.9052	2.39	4	61	3.5077	–	14
0.8973	2.35	4	125	3.6131	4.0216	18

to be fully justified as the polymer chains were found to comprise entirely of styrene repeat units, as described later.

3. Results and discussion

3.1. Copolymer compositions

From the NMR analyses, it is evident that MDO cannot be detected in the polymer chains even at very high feed ratios of MDO. This is demonstrated in the NMR spectrum shown in Fig. 2, for a polymer obtained from a monomer feed ratio of approximately 60 mol% MDO. The absence of any signal at 4.07 ppm corresponding to the methylene protons adjacent to the ester group in MDO is quite striking. These results seem inconsistent with previous data [4], indicating that the copolymerization of MDO with STY cannot be confirmed on the basis of this composition data.

3.2. Pulsed-laser polymerization data

Pulsed-laser polymerization (PLP) was used to evaluate the average propagation rate constant, $\langle k_p \rangle$, from the PLP molecular weight distributions via Eqs. (1) and (2)

$$\langle k_p \rangle = \frac{\nu}{[M]_{\mathrm{co}} t_f} \tag{1}$$

$$\nu = \frac{M_{\mathrm{inf}}}{m_{\mathrm{co}}} \tag{2}$$

$$[M]_{\mathrm{co}} = \frac{1000}{\dfrac{f_{\mathrm{MDO}} m_{\mathrm{MDO}}}{\rho_{\mathrm{MDO}}} + \dfrac{f_{\mathrm{STY}} m_{\mathrm{STY}}}{\rho_{\mathrm{STY}}}} \tag{3}$$

$$m_{\mathrm{co}} = F_{\mathrm{MDO}} m_{\mathrm{MDO}} + F_{\mathrm{STY}} m_{\mathrm{STY}} \tag{4}$$

where M_{inf} is the molecular weight at the inflection point; m_{co}, the average molecular weight of the repeat unit in the

Table 2
Polymerization conditions, molecular weights and propagation rate constants at 40°C

f_{MDO}	Initiator concentration $[I]$ ($\times 10^{-3}$ mol l^{-1})	Frequency (Hz)	Reaction time (min)	Primary inflection molecular weight (log M_{inf1})	Overtone inflection weight (log M_{inf2})	$\langle k_p \rangle$ (l mol^{-1} s^{-1})
0.0000	6.52	2	30	4.8617	5.1709	164
0.0000	6.52	4	15	4.5644	4.8664	165
0.1176	6.76	2	30	4.8153	5.1211	146
0.1176	6.76	4	15	4.5229	4.8204	149
0.2282	7.43	2	30	4.7678	5.068	130
0.2282	7.43	4	15	4.4683	4.768	130
0.4382	7.33	2	45	4.6313	4.9259	94
0.4382	7.33	4	20	4.3364	4.6421	95
0.6128	8.29	2	60	4.4691	4.7728	64
0.6128	8.29	4	25	4.1784	4.4825	65
0.8085	8.28	2	90	4.1682	4.464	31
0.8085	8.28	4	25	3.8838	4.1706	33
0.9384	7.51	2	120	3.6703	4.0115	10
0.9384	7.51	4	40	3.5711	–	16

Table 3
Polymerization conditions, molecular weights and propagation rate constants at 40°C and at ~50% dilution in toluene

f_{MDO}	Initiator concentration $[I]$ $(\times 10^{-2}\ \mathrm{mol\ l})^{-1}$	monomer concentration $[M]$ (mol l^{-1})	Frequency (Hz)	Reaction time (min)	Primary inflection molecular weight (log M_{inf1})	Overtone inflection weight (log M_{inf2})	$\langle k_p \rangle$ (l mol^{-1} s^{-1})
0.0000	1.80	4.398	1	120	4.8318	5.1462	148
0.0000	2.28	4.444	2	60	4.5138	4.8215	141
0.1228	2.67	4.422	1	120	4.7898	5.0948	134
0.1085	2.23	4.517	2	60	4.4842	4.7779	130
0.2227	2.75	4.480	1	120	4.7435	–	119
0.2152	2.25	4.490	2	60	4.4487	4.7070	120
0.4231	2.99	4.600	1	180	4.6081	4.9086	85
0.4243	1.83	5.801	2	90	4.3051	4.6224	67
0.6121	2.66	4.595	1	240	4.4418	4.7588	58
0.6192	2.91	4.666	2	125	4.1270	4.4367	55
0.8100	2.48	4.751	1	300	4.1300	4.4180	27
0.7894	2.87	4.677	2	180	3.8845	4.1730	31
0.9021	2.44	4.804	1	450	3.8454	4.1305	14
0.8677	2.22	4.644	2	255	3.6897	3.9900	20

polymer; m_{MDO} and m_{STY}, the molecular weights of MDO (114.14 g mol^{-1}) and STY (104.15 g mol^{-1}), respectively. F_{MDO}, F_{STY} and f_{MDO}, f_{STY} are the mole fractions of MDO and STY in the polymer and the comonomer mixture, respectively. The average comonomer concentration is given by $[\mathrm{M}]_{\mathrm{co}}$ (Eq. (4)) where ρ_{MDO} and ρ_{STY} are the densities of MDO and STY monomer, respectively. The monomer densities of STY where taken from the relationship $\rho_{\mathrm{STY}} = 0.9237–8.915 \times 10^{-4} T/°\mathrm{C}$. The densities of MDO were measured using a density bottle, over the range from 25 to 80°C and were found to fit the relationship; $\rho_{\mathrm{MDO}} = 1.04–9.02 \times 10^{-4} T/°\mathrm{C}$. Polymerization conditions, inflection points and the resulting average propagation rate constants are given in Tables 1–3. The PLP molecular weight traces were clearly bimodal and demonstrated the classical features of PLP, as shown in Fig. 3, indicating the absence of a significant transfer in these polymerization reactions. The low-molecular inflection points were found to be clear and distinct for all feed ratios of MDO with the precise values for υ markedly decreasing in value with increasing MDO in the feed (Fig. 3).

Initial inspection of the $\langle k_p \rangle$ data obtained for the copolymerization of MDO and STY, appears to indicate a simple dilution of styrene with the $\langle k_p \rangle$ values decreasing linearly with the amount of MDO added (Fig. 4). This is consistent with the NMR results that suggest that there is no incorporation into the backbone. This result was checked in a quantitative manner by comparing the experimental data with predictions based on a simple dilution effect and the terminal model based on the previously reported values for the

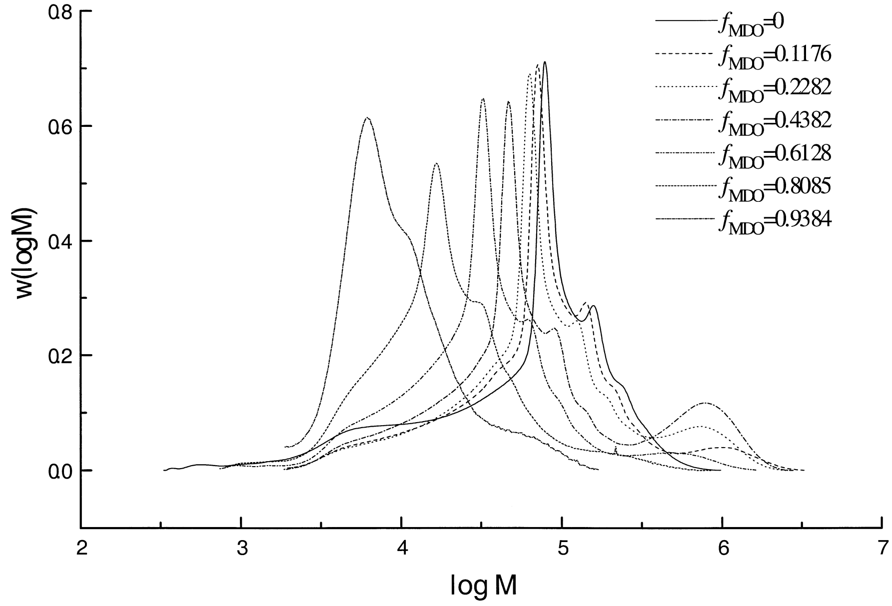

Fig. 3. Molecular Weight distributions ($w(\log M)$ vs $\log M$) for the PLP of MDO and STY at 40°C and $f = 2$ Hz.

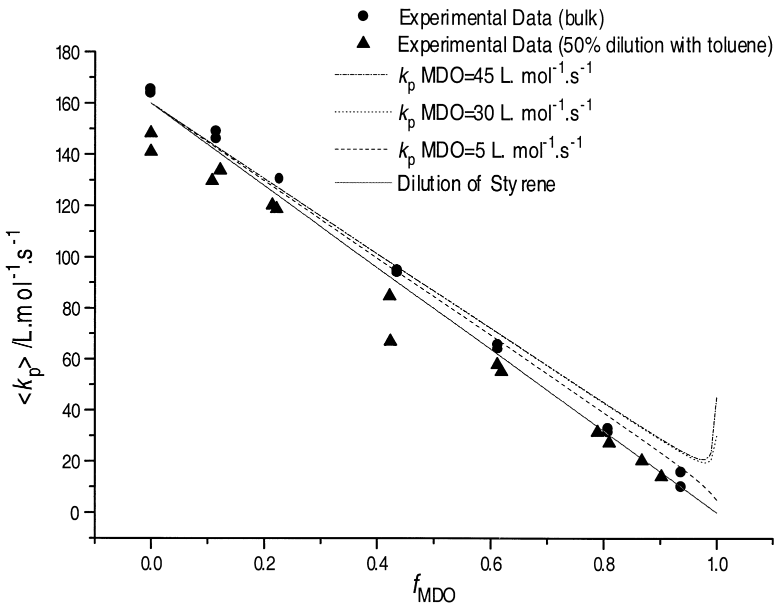

Fig. 4. Sensitivity analysis of terminal model fit for $\langle k_p \rangle$ at 40°C.

reactivity ratios for MDO and STY reported by Bailey et al. [4].

3.3. Terminal model fit

In order to assess the validity of the terminal model, it is necessary to estimate the homopropagation constant for MDO. This issue has been discussed in a previous paper [7] and preliminary high level ab initio molecular orbital calculations of the 5-membered analogue of MDO yielded an estimate for the propagation rate constant for this compound [8] given as Eq. (5). It is (at least initially) assumed that the value for MDO is likely to be of a similar order of magnitude

$$k_p \approx 1.0 \times 10^7 \exp\left(-\frac{30 \pm 5\ \mathrm{kJ\ mol^{-1}}}{\mathrm{R}T}\right) \tag{5}$$

Using Eq. (5), it is possible to estimate k_p for MDO around 45 l mol^{-1} s^{-1} at 40°C. These estimates have been used to appraise the terminal model predictions for the $\langle k_p \rangle$ values in the copolymerization of MDO with STY, as shown in Fig. 4 at 40°C (a similar result was obtained at 30°C). As the k_p estimates for MDO may be unreliable, a sensitivity analysis of the terminal model predictions at 30 and 40°C has also been performed — this is also shown in Fig. 4 for the 40°C data.

From the sensitivity analysis of the terminal model prediction, it is clear that changing the value of the k_p for MDO by one order of magnitude has little effect on the terminal model fit. It is clear that the $\langle k_p \rangle$ data is best described simply by a dilution of styrene by MDO, with MDO not participating in the polymerization. This is clearly shown by the agreement of the experimental data with a simple dilution model, as shown in Fig. 4. Here, the $\langle k_p \rangle$ for the copolymerization of MDO and STY is simply given by the relationship, $\langle k_p \rangle = f_{\mathrm{STY}} \times k_p^{\mathrm{STY}}$, where f_{STY} is the feed ratio of STY and k_p^{STY} is the homopropagation rate constant for STY. These PLP results are consistent with the NMR evidence revealing no incorporation of MDO into the polymer backbone.

4. Conclusions

From the measured propagation rate constants, it is clear that MDO does not undergo any measurable copolymerization with styrene. This has been confirmed via NMR analyses, which indicate an absence of MDO units in the backbone of the polymer. The copolymerization data are entirely consistent with a simple explanation that MDO merely acts as an inert diluent for styrene homopolymerization.

Acknowledgements

We wish to thank the Australian Research Council for generous funding and we acknowledge the receipt of an APA Scholarship to L.M.M.

References

[1] Acar MH, Nambu Y, Yamamoto K, Endo T. J Polym Sci, Polym Chem Ed 1989;27:4441–3.
[2] Bailey WJ. Free radical ring-opening polymerization. In: McGrath JE, editor. Ring-opening polymerization: kinetics mechanisms and synthesis, Washington, DC: American Chemical Society, 1985.
[3] Bailey WJ. Ring-opening polymerization. In: Eastmond GC, Ledwith A, Russo S, Sigwalt M, editors. Comprehensive polymer science, vol. 3. London: Pergamon, 1989. p. 283–319.

[4] Bailey WJ, Ni Z, Wu S-R. J Polym Sci, Polym Chem Ed 1982;20:3021.

[5] Bailey WJ, Chen PY, Chen S-C, Chiao W-B, Endo T, Gapud B, Kuruganti V, Lin Y-N, Ni Z, Pan C-Y, Shaffer SE, Sidney L, Wu S-R, Yamamoto N, Yamazaki N, Yonezawa K, Zhou L-L. Makromol Chem, Macromol Symp 1986;6:81–100.

[6] Endo T, Okawara M, Bailey WJ, Azuma K, Nate K, Yokono H. J Polym Sci, Polym Lett Ed 1983;21:373.

[7] Endo T, Yokozawa T. Free radical ring-opening polymerization. In: Mijs WJ, editor. New methods for polymer synthesis, New York: Plenum Press, 1992. p. 155–77.

[8] Heuts JPA, Iskander GM, Davis TP. Paper presented at the 22nd Australasian Polymer Symposium, Auckland, 1997.

[9] Jin S, Gonsalves KE. Macromolecules 1997;30:3104–6.

[10] Morris LM, Harrisson SA, Davis TP, Chaplin RP, King GC. Submitted for publication.

[11] Roberts GE, Coote ML, Heuts JPA, Morris LM, Davis TP. Macromolecules 1999;32:1332–40.