

Homo-oligomerization of Maleic Anhydride in Nonpolar Solvents: A Kinetic Study of Deviations from Nonlinear Behavior

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ABSTRACT: Deviation from nonlinear first order polymerization kinetic models is usually observed for cases where steric effects are dominant. A kinetic model was developed for the homo-oligomerization of bulky maleic anhydride units. Factors affecting the kinetics of homo-oligomerization of maleic anhydride have also been studied using two different initiators, azoisobutyronitrile (AIBN) and benzoyl peroxide, at 10 mol % concentrations in two different solvents *o*-xylene and toluene. Maleic anhydride polymers having a number average molecular weight by SEC, between 300 and 900, and a polydispersity of between 1.0 and 2.0 were observed, and data were justified by the model. The molecular weight of the polymers increased with

the conversion, and steric effects dominated at higher molecular weight as observed from the decrease in magnitude in the corresponding termination rate constants. The model values of conversion were compared with experimental data and cross verification of the model was done using molecular weight calculations. The present model represents the data with an average error of less than 5% over the entire experimental range. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3404–3412, 2006

Key words: atom transfer radical polymerization; modeling; degree of polymerization; gel permeation chromatography; initiators

INTRODUCTION

Much attention has recently been devoted to the synthesis of water-soluble polymers that have a wide range of application in industry; one of the most important being as an antiscalant.^{1–4} Maleic anhydride is a convenient starting point for synthesizing such water-soluble polymers that can be put to use in a multitude of applications.^{5–8}

In maleic anhydride, the presence of both an electron acceptor double bond and an anhydride moiety renders it susceptible to free radical, addition, and condensation type polymerizations. However, until the 1960s it was believed that this versatility did not include the production of homopolymers. In fact because of its reluctance to polymerize due to its bulky anhydride moiety, maleic anhydride was often used as an example of the concept of steric hindrance and polar effects impeding the homo-oligomerization of 1,2-disubstituted olefins. In 1961, however, it was shown that maleic anhydride could be homopolymer-

ized with γ - and UV radiation^{9–12}, resulting in 14–28% yield. Polymaleic anhydride can also be produced by the action of ionic catalysts and organic bases.^{13–22} Ionic-type polymerization of maleic anhydride does not produce a commercial polymer.

Maleic anhydride polymerizes spontaneously when heated to 100–170°C under a pressure above 2 GPa (20,000 atm).²³ Shock waves generated by detonations, promote maleic anhydride polymerization due to intense transient high pressure and temperature.^{24,25} There are several publications on homo-oligomerization of maleic anhydride by electrochemical^{26,27} and electromagnetic^{28,29} methods. However, yields were low and intricate details pertaining to the homo-oligomerization kinetics have remained unexamined.

Maleic anhydride can be polymerized by the action of free radical catalysts.^{30–37} The first polymerization of maleic anhydride with free radical initiators gave a polymer with a DP of 25–29.³⁸ Attempts to polymerize molten maleic anhydride with lauroyl peroxide or azoisobutyronitrile (AIBN) were not successful.³⁹

Hoechst⁴⁰ disclosed a process for the preparation of polymaleic anhydride, in which maleic anhydride is polymerized in an inert solvent, in the presence of an organic percarbonate or diacyl peroxide, with amounts ranging from 2 to 40 wt % by weight, based on maleic anhydride.

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A similar study was undertaken by Jones et al.⁴¹ on the homo-oligomerization of maleic anhydride in xylene as the solvent, which contains up to 99% of *o*-xylene, di-*tert*-butyl peroxide being used as the polymerization initiator, in an amount of from 15 to 40% by weight, based on maleic anhydride. The polymers prepared by this process also contain a substantial amount of unpolymerized maleic anhydride.

The homo-oligomerization of maleic anhydride occurs readily in the presence of a free radical precursor at high concentration³¹ or having a short half-life at the reaction temperature, and is promoted when a photo sensitizer is also present.⁴² However, the polymer yield is low and the polymer so prepared contains substantial amount of unpolymerized maleic anhydride.

The foregoing discussion clearly shows that while there is considerable information available on the synthesis and structural aspects of polymaleic anhydride, there is little information on the overall justification of kinetics of the reactions. Therefore, the present investigation was undertaken to study the kinetics of the homo-oligomerization of maleic anhydride and to develop a mathematical model capable of fitting the conversion and molecular weight as a function of time, and to determine the effects of different initiator and different solvents on the molecular weight of the polymer. The developed relation would be used in later studies to determine the time required to attain a certain low molecular weight polymaleic anhydride that can be used in water-soluble polymer applications.

EXPERIMENTAL STUDY

Maleic anhydride (mp 56°C) obtained from Sigma (St. Louis, MO) was recrystallized from reagent grade benzene and dried under vacuum at room temperature. Benzoyl peroxide (BPO) and AIBN obtained from Aldrich (Milwaukee, WI) were crystallized from reagent grade methanol prior to use. All other solvents were purified by conventional methods. The solvent used for spectroscopic measurements was of spectral grade and obtained from Sigma.

Molecular weight measurements of polymaleic anhydride were carried out by high temperature size exclusion chromatography (SEC). The chromatograph was a Waters 150C ALC/GPC system equipped with three columns (3 styragel HR 5 μm columns of 50, 10³, and 10⁴ Å). A differential refractometer detector was used for recording and analyzing the signal. The permeation solvent was THF. The concentration was in the range 4–6 mg/L and the injection volume was 200 μL . A polystyrene calibration was used for SEC analysis.

¹³C NMR spectra were obtained using a Bruker-AM 400 NMR spectrometer. The samples were dissolved

in CDCl₃ or acetone-*d*₆ and the shifts were referenced to tetramethylsilane. IR spectra were recorded with Perkin-Elmer 16-PC FTIR spectrometer using KBr discs, in the range of 4000–400 cm⁻¹.

All polymerization studies were conducted with 0.0617 mol monomer (maleic anhydride) in 250 mL of solvent *o*-xylene or toluene under N₂ atmosphere at temperatures of 110 and 143°C. Two different initiators AIBN and benzoyl peroxide (BPO) were used for homo-oligomerization at 10 mol % concentration. The progress of the reaction was followed by recording the disappearance of the monomer maleic anhydride; samples were withdrawn from the reaction mixture their maleic anhydride contents determined by LC. The increase in the molecular weight of the polymer was determined by gel permeation chromatography.

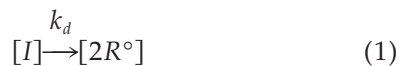
A typical polymerization was carried out by weighing 0.0617 mol of maleic anhydride and 210 mL of solvent, which were then refluxed under N₂ atmosphere. Initiator dissolved in 40 mL of solvent was added for a period of 4 h. Refluxing was continued for further 8 h and the polymer was allowed to separate from the solution. Excess solvent was distilled off and a sample of the polymer so obtained was recrystallized in CHCl₃. The product was a white colored crystalline polymaleic anhydride.

Kinetic model

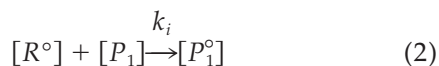
Homo-oligomerization of maleic anhydride in an inert solvent proceeds via a free radical mechanism. A free radical chain polymerization reaction mechanism usually results in a first order kinetic expression for which a plot of $\log ([M]_0/[M]_t)$ against time gives a straight line that usually fits most experimental data well.^{27,28} The first-order kinetic expression results from the simplifying assumption that the rate constants for chain propagation and termination are independent of chain length, and hence, any steric effects are negligible. However, this was not the case for the experimental runs undertaken in this study. A first-order rate expression was followed for a short reaction time but this failed to provide a comprehensive fit for the entire duration of the experiment. Hence, in the present study, we have derived a rate expression for radical chain polymerization where the rate constants are dependent on steric effects, due to the nature of the bulky anhydride moiety.

In the kinetic model, a radical chain polymerization consisting of a sequence of four steps, decomposition, initiation, propagation, and termination, is considered and represented in the following steps:

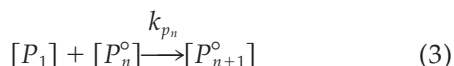
1. Initiator thermal decomposition



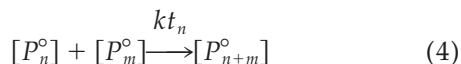
2. Free radical initiation



3. Propagation sequence



4. Termination by coupling sequence



Here I , R° , P_1 , P_1° , P_2 , P_2° , P_3 , P_3°, \dots, P_{11} represent the concentration of initiator, initiator radical, maleic anhydride monomer, monomer radical, dimer, dimer radical, trimer, trimer radical and so on. The rate constants k_i , k_{p_n} , and k_{t_n} apply to the initiation, propagation, and termination by coupling reactions, respectively.

Two different initiators AIBN and BPO were studied at 10 mol % concentration in two separate solvents, *o*-xylene and toluene. Propagation occurs by bimolecular reaction involving the successive addition of maleic anhydride molecules. The termination reaction is assumed to take place predominately by the coupling of growing chains or coupling between growing chains and initiator radical, the latter is considered a minor contributor to the process and is neglected.

In the most general case, the rate constants for different free radical polymerization reactions should be different and dependant on molecular weight, temperature, pressure, and type of reaction. This would result in two general terms in the rate equations, a propagation term, P , and a termination term, T , whose magnitudes are as follows:

$$|P_i| = \sum_{j=1}^{i+1} k_{p_j} P_1 P_{j-1} \quad (5)$$

$$|T_i| = \sum_{j=1}^{i-1} k_{t_j} P_j^\circ P_{i-j}^\circ \quad (6)$$

In the case that steric factors are considered,⁴³ we assume that the propagation and termination rate constants in P and T have the following relations: $\frac{k_{p_{i+1}}}{k_{p_i}}$

$= \varepsilon_{p'}$, and $\frac{k_{t_{i+1}}}{k_{t_i}} = \varepsilon_t$. Comparing the two terms, the rate of reaction of two radicals is higher than that of a radical and a monomer or $k_{t_i} > k_{p_i}$ for small i . On the other hand, the steric effects tends to increase with molecular weight, diluting the effects of radical-radical and radical-monomer interaction. Hence, $\varepsilon_t \leq \varepsilon_{p'}$. Comparing the magnitudes of both k_t and k_p in T and P , $\lim_{n \rightarrow \infty} k_{t_n} \rightarrow 0$ faster than $\lim_{n \rightarrow \infty} k_{p_n} \rightarrow 0$. Hence, in a given range of i , in P and T , starting at $i = 1$, k_{p_i} is considered constant, while k_{t_i} is variable. This reduces the propagation and termination terms to the following expressions:

$$|P_i| = k_p \sum_{j=1}^{i+1} P_1 P_{j-1} \quad (7)$$

$$|T_i| = \sum_{j=1}^{j < i-j} k_{t_j} P_j^\circ P_{i-j}^\circ + \sum_{j \geq i-j}^{i-1} k_{t_{i-j}} P_j^\circ P_{i-j}^\circ \quad (8)$$

No simplifications were used for the dissociation or initiation steps. However, the propagation and termination steps reduce to the following rate expression forms:

1. Initiator thermal decomposition

$$-\frac{d[I]}{dt} = k_d[I] \quad (9)$$

2. Free radical initiation

$$\frac{d[R^\circ]}{dt} = 2k_d[I] - k_i[R^\circ][P_1] \quad (10)$$

3. Propagation sequence steps

$$\frac{d[P_i^\circ]}{dt} = k_p \sum_{j=1}^{i+1} P_1 P_{j-1}^\circ - \sum_{j=1}^{j \leq i-j} k_{t_j} P_j^\circ P_{i-j}^\circ - \sum_{j \geq i-j}^{i-1} k_{t_{i-j}} P_j^\circ P_{i-j}^\circ \quad (11)$$

4. Termination by coupling sequence

$$\frac{d[P_i]}{dt} = \sum_{j=1}^{j < i-j} k_{t_j} P_j^\circ P_{i-j}^\circ - \sum_{j \geq i-j}^{i-1} k_{t_{i-j}} P_j^\circ P_{i-j}^\circ \quad (12)$$

In deriving the rate equations from the rate expressions above, a tacit assumption is made that oligomers up to DP = 11 are present in the reaction system. This assumption is based on the molecular weight obtained from SEC. The values of rate constant k_i is assumed for the initiation reaction, k_p for propagation and k_{t1} , k_{t2} , k_{t3} , and k_{t4} for termination by coupling due to monomer, dimer, trimer, and tetramer radicals respectively. Then the corresponding rate equations are as follows:

TABLE I
Conditions and Results for the Homo-oligomerization of Maleic Anhydride

Entry	MA (mol/L)	Solvent	Initiator	Initiator composition (mol %)	Conversion (%)	M_w	M_w
1	0.247	O-xylene	AIBN	10	80.68	818 ^a	810 ^b
2	0.247	O-xylene	BPO	10	70.01	764	847
3	0.247	Toluene	BPO	10	44.59	430	430

AIBN, azoisobutyronitrile; BPO, benzoyl peroxide.

^a Molecular weights theoretically calculated by model in eq. (21).

^b Molecular weights obtained from SEC.

$$-\frac{d[I]}{dt} = kd[I] \quad (13)$$

$$\frac{d[R^\circ]}{dt} = 2k_d[I] - k_i[R^\circ][P_1] \quad (14)$$

$$-\frac{d[P_1]}{dt} = k_i[R^\circ][P_1] + k_p P_1 [P_1^\circ + P_2^\circ + \dots P_{10}^\circ] \quad (15)$$

$$\frac{d[P_1^\circ]}{dt} = k_i[R^\circ][P_1] - k_p[P_1][P_1^\circ] - k_{t1}P_1^\circ[P_1^\circ + P_2^\circ + \dots P_{10}^\circ] \quad (16)$$

$$\frac{d[P_2]}{dt} = \frac{1}{2}k_{t1}[P_1^\circ][P_1^\circ] \quad (17)$$

$$\frac{d[P_2^\circ]}{dt} = k_p P_1 [P_1^\circ - P_2^\circ] - k_{t1}[P_1^\circ][P_2^\circ] - k_{t2}P_2^\circ[P_2^\circ + P_3^\circ + \dots P_9^\circ] \quad (18)$$

$$\frac{d[P_3]}{dt} = kt_1[P_1^\circ][P_2^\circ] \quad (19)$$

$$\frac{d[P_3^\circ]}{dt} = k_p P_1 [P_2^\circ - P_3^\circ] - k_{t1}[P_1^\circ][P_3^\circ] - k_{t2}[P_2^\circ] \times [P_3^\circ] - k_{t3}P_3^\circ[P_3^\circ + \dots P_8^\circ] \quad (20)$$

These 24 differential equations were solved numerically with the initial condition $P_1 = [MA]_0$, $I = [I]_0$ and the concentration of all the remaining radicals and oligomers concentrations as zero. Numerical values for the concentration of the different mer species (N_i) and their molecular weights (M_i) were then used to predict the weight average molecular weight (M_w), defined by eq. (21).

$$M_w = \frac{\sum_{i=1}^{DP} N_i M_i^2}{\sum_{i=1}^{DP} N_i M_i} \quad (21)$$

The computed values of monomer concentration were compared with the experimental values and the five rate constants optimized using a differential algebraic optimization technique.⁴³ The present model represents the data with an acceptable accuracy, with an average error between experimental and computed values of less than 5% for the entire experimental range. It fitted the data well and justified the proposed reaction mechanism.

RESULTS AND DISCUSSION

Homo-oligomerization of maleic anhydride was carried out in both polar solvent (DMF) and nonpolar solvent (toluene, *o*-xylene and THF), however, more positive results were obtained in nonpolar solvents. Polymerization in THF and DMF yielded a dark oily substance, which was difficult to purify. The product

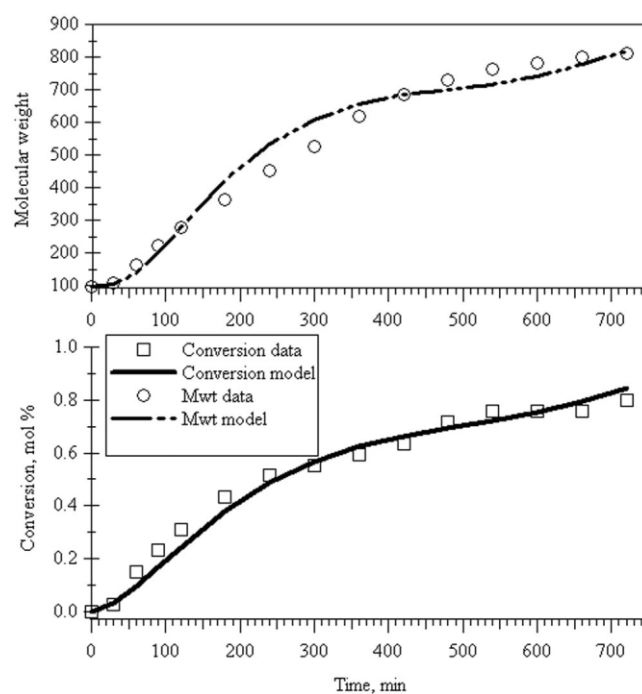


Figure 1 (a) Conversion versus reaction time of maleic anhydride in *o*-xylene using AIBN initiator. (b) Weight averaged molecular weight versus reaction time of polymaleic anhydride.

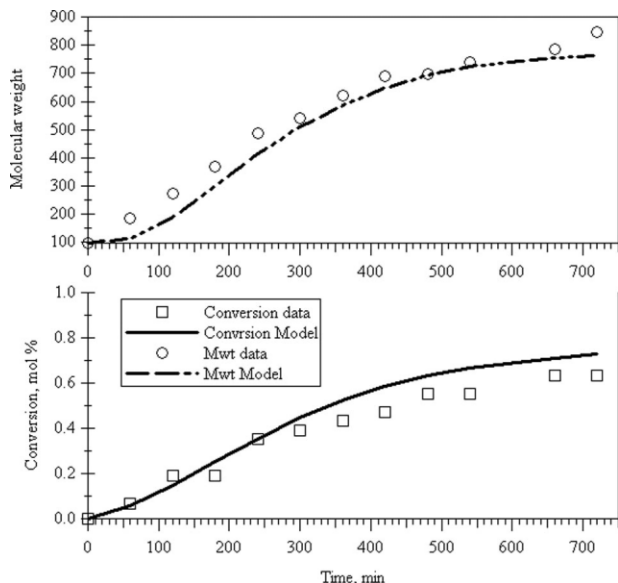


Figure 2 (a) Conversion versus reaction time of maleic anhydride in *o*-xylene using BPO initiator. (b) Weight averaged molecular weight versus reaction time of polymaleic anhydride.

obtained in toluene was an off-white solid with poor yield. Maleic anhydride polymerized effectively in *o*-xylene. This could be attributed to higher decomposition rate of AIBN and BPO in *o*-xylene and toluene in the range 2.75×10^{-2} – 3.65×10^{-3} compared to 6.5×10^{-5} – 8×10^{-6} for other two solvents.⁴⁴ Further-

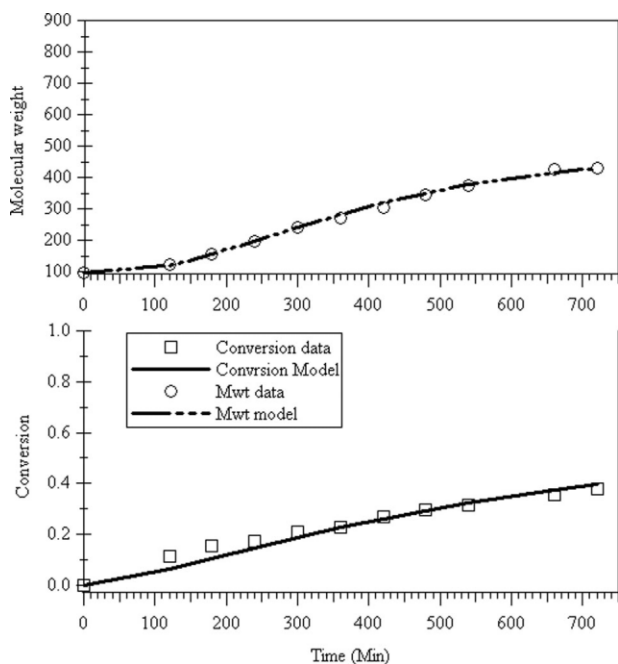


Figure 3 (a) Conversion versus reaction time of maleic anhydride in toluene using BPO initiator. (b) Weight averaged molecular weight versus reaction time of polymaleic anhydride.

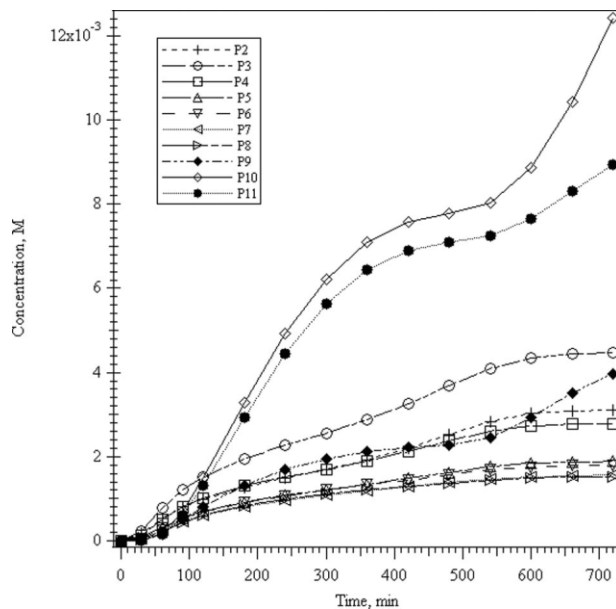


Figure 4 Simulation results of polymaleic anhydride oligomer concentration versus time initiated by AIBN (10 mol%) in *o*-xylene.

more, the formation of resonance stabilized benzyl free radicals which is better stabilized in *o*-xylene than in toluene due to presence of extra methyl group further justify the high yield of polymer in *o*-xylene. A detailed study of the solvent effect is the foal of currently ongoing work. Results of the experiments conducted are given in Table I.

Figures 1–3 compare the theoretical polymaleic anhydride production with that of the experimental measurements. The experimental values agreed well

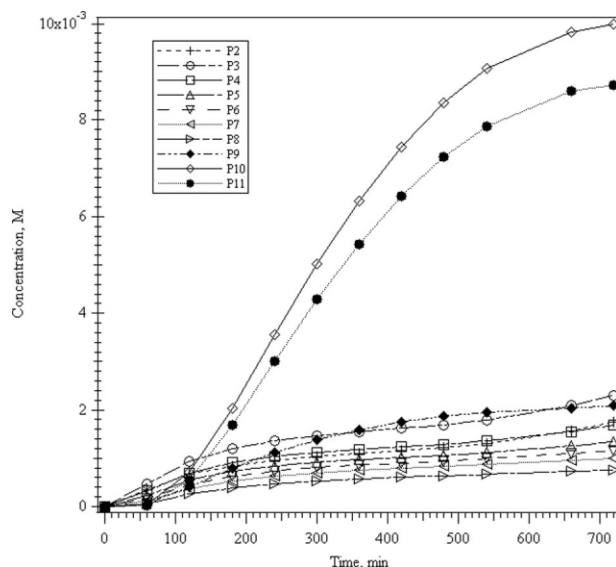


Figure 5 Simulation results of polymaleic anhydride oligomer concentration versus time initiated by BPO (10 mol%) in *o*-xylene.

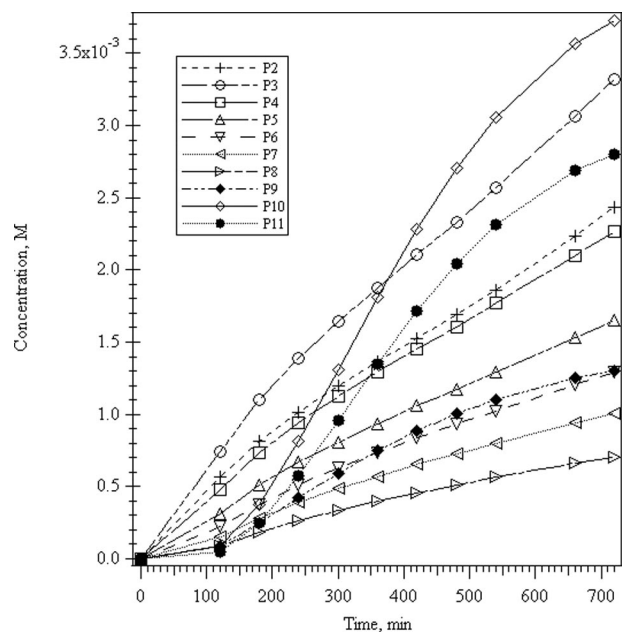


Figure 6 Simulation results of polymaleic anhydride oligomer concentration versus time initiated by BPO (10 mol%) in toluene.

with the theoretical values obtained from the present model indicating that the model is followed by free radical chain polymerization of maleic anhydride. The model was cross justified with the data from molecular weight measurements which further indicated a good match between the stated model and the experimental data as shown in parts (b) of the figure.

Figures 2 and 3 compare conversion and molecular weight in *o*-xylene and toluene at 10 mol % initiator (BPO) concentration. Clearly, a higher conversion and molecular weight was observed in *o*-xylene than in toluene. Comparing the results of polymerization using BPO with those of AIBN, it is observed that greater conversion and higher molecular weight are attained using AIBN rather than BPO under similar reaction conditions.

Variation of weight average molecular weight M_w of the resulting polymaleic anhydride with time gives an indication of the influence of initiator concentration on the course of reaction. Samples obtained in the pres-

ence of AIBN at 10 mol % resulted in a M_w of 810 at 80% conversion (Fig. 1) and a M_w of 847 at 65% conversion for the BPO (Fig. 2) at the same initiator concentration. This indicates that rapid polymerization in AIBN results in a product of lower molecular weight and higher conversion. The M_w values obtained in toluene are quite low compared to those in *o*-xylene and the conversion is half of that of AIBN, indicating inefficient initiation in toluene. There was good agreement between the theoretically predicted values^{45,46} for M_w and those experimentally obtained by SEC.

Figure 4 shows the concentration of various oligomers as a function of time using AIBN in *o*-xylene. It indicates maximum concentrations of P_{10} and P_{11} (DP = 10–11) whereas the concentration of P_2 – P_5 have reduced to 1.23×10^{-3} – 2.2×10^{-3} mol. A sharp increase (production) in the monomer radical concentration is observed in a 60 min period, whereas dimer, trimer and rest of the radical concentrations show a gradual increase. Consumption of monomer and dimer radicals is faster, indicating enhanced propagation, which is further justified by a propagation rate constants (k_p) that is higher than the values of BPO in *o*-xylene and toluene.

A slow propagation reaction is indicated in Figure 5 for BPO in *o*-xylene. There is a small increase in monomer and dimer radicals, and after 8 h of reaction, the dimer and trimer radicals show a gradual decrease in concentration while the rest of the oligomer radicals are increasing. This is indicative of slow initiation and propagation, and is further confirmed by the plot of oligomer concentrations. Figure 5 that show the highest concentration of P_{11} in the range 10.18×10^{-3} for BPO compared with 12×10^{-3} mol in AIBN. The results of a similar study with BPO in toluene is shown in Figure 6. After 10 h of refluxing the highest concentration of P_{10} is in the range 3.5×10^{-3} . In the BPO/toluene system, a gradual decrease is observed in monomer radical concentration after 5 h, whereas in the BPO/*o*-xylene system a decrease is observed after 2 h. By way of comparison, the AIBN/*o*-xylene system monomer radical concentration starts decreasing after 1 h. This indicates inefficient initiation in toluene compared to *o*-xylene.

TABLE II
Rate Constants and Corresponding Model Relative Error for Homo-oligomerization of Maleic Anhydride in Different Solvents and Initiator Types at 10 mol % Concentration

Initiator	Solvent	k_i	k_p	k_{t1}	k_{t2}	k_{t3}	k_{t4}	Relative model error % ^a
AIBN	O-xylene	0.0016	0.5848	41.9021	4.0574	37.7673	35.9410	3.10
BPO	O-xylene	0.0010	0.4567	46.0962	9.1560	20.0129	0.0083	6.10
BPO	toluene	0.0005	0.2728	47.5556	5.0548	14.4957	0.1125	1.70

$$^a \text{Error \%} = \frac{\text{Calculated} - \text{Experimental value}}{\text{Calculated value}}$$

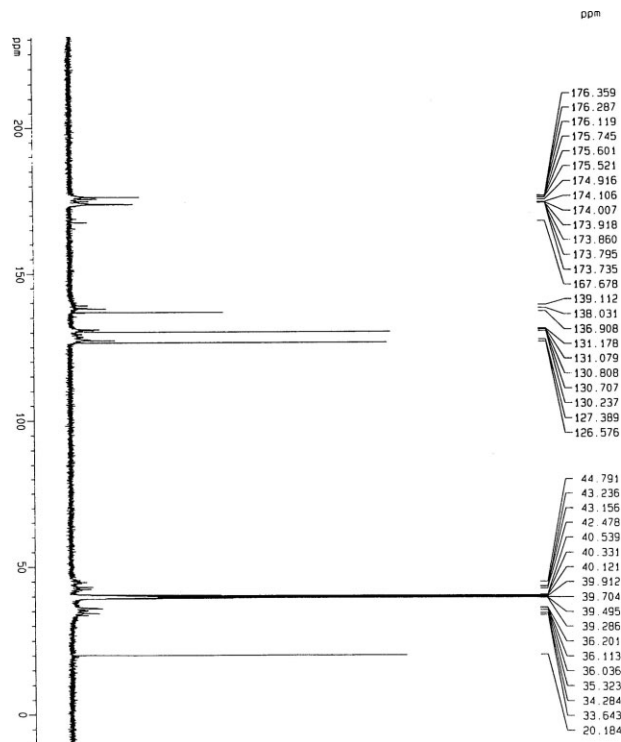


Figure 7 ^{13}C NMR spectrum of polymaleic anhydride.

The rate constants for initiation, propagation and termination for different solvents and initiator are given in Table II. The rates are dependent upon solvent, initiator and initiator concentration. Higher value for initiation and propagation rate constant are observed for AIBN than those for BPO. Besides, the

rate constants for termination by coupling due to monomer radical is higher compared to other radicals. As the molecular weight of the oligomers increase, the steric effects will dominate resulting, generally, in a lower termination rate constant, which is observed in Table II.

Polymer characterization

A ^{13}C NMR spectrum of the polymaleic anhydride is shown in Figure 7. Peaks in the spectra are divided into four groups: the first group, from 30 to 45 ppm, the second from 125 to 130 ppm and the third from 135 to 139 ppm and the fourth group from 173 to 177 ppm.⁴⁷ Isolated peaks are located at 20 and 167 ppm. The 20 ppm peak is attributed to the methyl groups within isobutyl groups or to the terminal methyl group of aliphatic alkanes. The peak located between 30 and 45 ppm corresponds to the methylene groups of aliphatic alkanes. These two groups of peaks (20 ppm and 30–45 ppm groups) could originate from the radical initiator which contains such aliphatic alkane groups. The peaks located between 125 and 130 ppm can be attributed to maleic acid while those situated between 135 and 140 ppm are due to MA ($C\alpha$ of the carbonyl in both the case). The isolated peak at 167 ppm can be attributed to the carbonyl of maleic anhydride or maleic acid. Finally the peaks at 173–177 ppm are due to the carbonyl group associated with succinic anhydride.

Termination by dismutation can lead to saturated (succinic type) or unsaturated (maleic or fumaric type) end groups.⁴⁸ Additional difficulties can be due to the

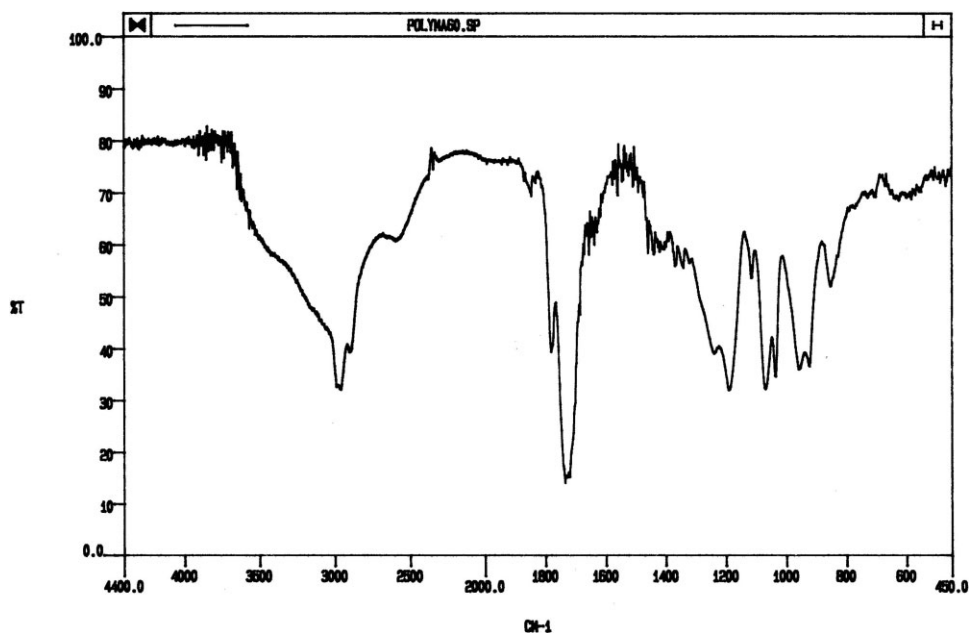


Figure 8 FTIR spectrum of polymaleic anhydride.

possible transformation of some anhydride functions into carboxylic acid functions with water contamination during the preparation or in deuterated DMSO. All these possibilities agree with the proposed attribution of the observed peaks.

The FTIR spectrum (Fig. 8) of the polymer shows two absorption bands between 1700 and 1800 cm^{-1} . Thus, are due to vibrations of carbonyl group and are quite similar to those obtained by various initiation methods in earlier studies.^{15,26,27,42} Figure 9 shows the low molecular weight SEC analysis of polymaleic anhydride. As often observed in the case of the analysis of oligomers of low molecular weight by SEC, the chromatogram shows different peaks relatively well separated and a tail on the high molecular mass side.

The attribution of the first peak of the lowest molecular mass can be achieved by considering Figure 10, which represents a low molecular weight SEC chromatogram of maleic anhydride. Consequently, in Figure 9, peak 2 could be due to the dimer, peak 3 to the trimer, peak 4 to the tetramer, and so on. The broad peak on the highest molecular mass side should correspond to a small portion of higher oligomers.

CONCLUSIONS

This article examines the effect of the steric factor in the oligomerization steps of MA. The model shows

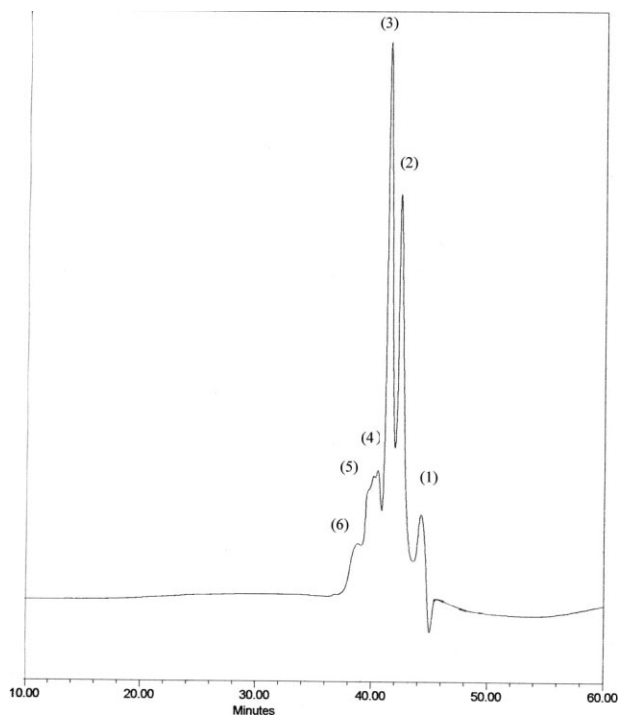


Figure 9 Low molecular weight SEC chromatogram of polymaleic anhydride: peak (1) maleic anhydride monomer; peak (2) maleic anhydride dimer; peak (3) maleic anhydride trimer; peak (n) polymaleic anhydride *n*-mer.

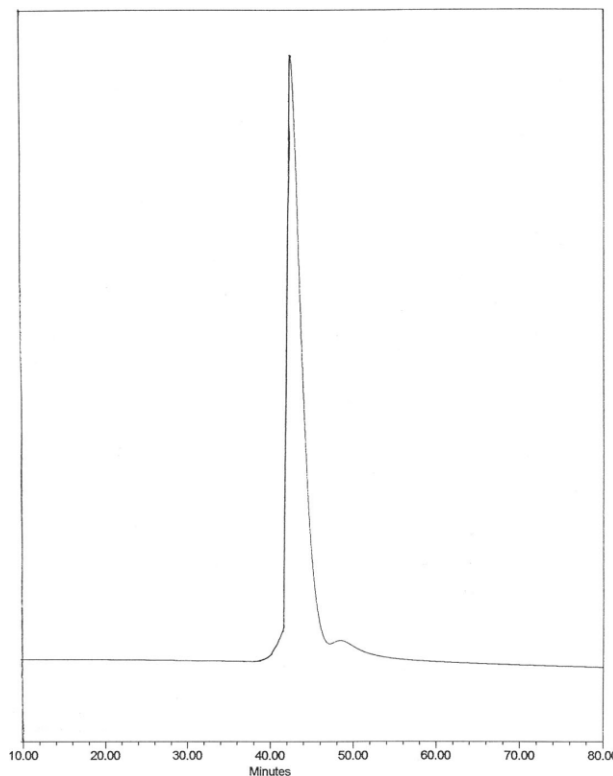


Figure 10 Low molecular weight SEC chromatogram of maleic anhydride monomer.

that the effect of the bulky group is on the termination rate constants as shown by the simulation results. It is clear that for the case of bulky oligomers, the general assumption that the termination step rate constants are equal and independent of nature of the free radical species is not valid.

In addition, this model has shown that six different rate constants, k_i for initiation reaction, k_p for propagation reaction, k_{t1} termination rate constant due to monomer radical, k_{t2} , k_{t3} , and k_{t4} termination due to dimer, trimer and tetramer radicals respectively, can be calculated with great precision.

Although the reaction was carried out in both polar solvent (DMF) and nonpolar solvent (toluene, *o*-xylene and THF), better results were obtained in nonpolar solvent *o*-xylene at higher temperature.

Two initiators AIBN and BPO at 10 mol % concentrations were employed in the homopolymerization of maleic anhydride. Conversion as high as 80% in AIBN and 65% in BPO was observed in *o*-xylene where as in Toluene only 40% conversion was found after 12 h of refluxing. Our data shows that AIBN is a more suitable initiator over BPO.

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