The Kinetic Modeling of a Bulk Diallylterephthalate Polymerization

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A mathematical model describing free radical polymerization of diallyl terephthalate in a bulk, which exhibits strong diffusion limitations from the beginning of the reaction, was developed. The diffusion limitations are viewed as an integral part of the chain propagation and termination processes. The influence of temperature and initiator loading on the reaction process was investigated. Initiator decomposition rate constants were obtained from special experiments, by using the dead end theory. The ratios of degradative and the effective chain transfer rate coefficients to propagation rate coefficients were in range between 0.01 to 0.06 for $k_{\mathrm{Deg}}/k_{\mathrm{p}}$ and between 0.001 to 0.008 for $k_{\mathrm{Eff}}/k_{\mathrm{p}}$. Ratios were evaluated from GPC molar mass measurements. The kinetic parameters were estimated by fitting the experimentally obtained conversion measured by FTIR for various initiators in temperature range from 50 °C to 150 °C by using peroxide initiators CHPC and DCPO. Activation energies estimated from kinetic modeling were 36.9 kJ mol^{-1} for propagation and 144.7 kJ mol^{-1} for termination, respectively.

Keywords:
Kinetic modeling, Fourier transform infrared (FTIR), bulk polymerization, diallyl phthalate, diallyl terephthalate.

Introduction

Diallyl phthalate (DAP) is a monomer, which is employed as a characteristic engineering plastic material in the electronic and optic industries. The polymerization behavior of DAP exhibits general characteristics of allyl polymerization with two reactive functional groups. Allyl polymerization has not received as much attention as the corresponding vinyl polymerization, since it is more difficult to polymerize allyl monomers using free radical initiators than vinyl ones.[1,2] This difficulty was explained by side transfer reactions, i.e. the degradative and the effective chain transfers. The side cyclization reactions are another aspect of the polymerization of diallyl diesters.[3,4,5]

There are many models in literatures that provide mechanistic details for gelation kinetics and the effect of gel structure on the kinetics,[6-15] however, they demand of knowing some data like free volumes and critical conversions, which are not available in the literature for diallyl phthalates. The developed kinetic model is assembled from others work,[9,16-18] however, this approach has not been used for kinetic modeling of more complicated systems such as diallyl phthalates. In addition, the authors are fully aware of the fact, that some investigators[6a,6b,12-14,16,19,20] have suggested, that free volume theory may be used for incorporating the effect of diffusion control into the expression for the rate constants of propagation and termination. However, in practice, were unable to measure the necessary data for calculation, therefore, the CCS [16] algorithm for kinetic modeling was used, which does not need free volume data.

Numbers of detailed mathematical models for bulk free radical polymerization are proposed in literature for MMA, styrene and other simple monomer systems,[6a,6b,7] On the other hand, the proposed kinetic model, describing more complicated polymerization (DAP), and containing adjustable parameters for fitting model predictions to experimental data with the parameters, with clear and physical meanings, cannot be found in the available literature.[8-15]

The purpose of this work is: (i.) to investigate the bulk free radical polymerization of DAT over the complete crosslinking range, from the initial liquid state, through the gel state and to the final glassy state; (ii.) to develop a detailed kinetic model describing an isothermal batch free radical bulk polymerization process; (iii.) to determine kinetic rate constants and their dependencies on temperature and transport properties.

Experimental

The monomer diallyl terephtalate (DAT) from Daiso Co. Ltd. and commercial peroxide initiators

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dicyclohexyl peroxydicarbonate (CHPC) from Peroxide Chemie Gmbh and dicumyl peroxide (DCPO) from Hercules, were used.

Samples of approximately 50 mg of monomer were prepared in tubes at 20 °C. An initial amount of the initiator was added to DAT separately, mixed in nitrogen atmosphere and then put in a water bath. The initiator mass fraction varied between (w = 0.1 and 8 %). The polymerization process was carried out between 50 °C and 150 °C. At different reaction times, the samples were quenched on ice and prepared for an analysis.

The C=C bond conversion was measured using attenuated total reflection technique (ATR) with the use of well known Harrick's relation, and taking into account the dependence of the depth of penetration to wavelength and refractive indexes of both polymer samples and Zn/Se crystal. ATR allows measurements of liquid and gel samples, while the KBr technique was used for the measurements of solid samples. Fourier Transform Infrared (FTIR) spectra were obtained by Perkin-Elmer SPECTRUM 1000 spectrometer using horizontal Zn/Se crystal ATR accessory with the angle of incidence 45°. The spectra were recorded at room temperature in nitrogen atmosphere after 32 scans at 2 cm^{-1} resolutions for ATR and KBr technique. The reference spectra were taken, using blank Zn/Se crystal and blank KBr cell at the same conditions. The experiments were carried out in three parallels and each conversion point was recorded from 3 to 15 times per experiment. The average C=C bond conversions were calculated from these sets of data obtained.

The molar mass were measured by Perkin Elmer GPC PL gel mixed E column, with the pore diameter of 260 nm. Tetrahydrofurane (THF) was used as an eluent for different degrees of polymerization. Polystyrene (PS) standards were used for the calibration of molar mass.

Kinetic modeling

Developed kinetic model is based on well-known principles of free radical polymerization presented in various standard polymerization text books and extensive papers.[12,13,22-26] In most developed models gel effect is the critical break point. However, for modeling the reactions the approach developed by *Chiu* et al.[16] (CCS), which incorporates the diffusion limitations from the beginning of the reaction without critical break point, is appropriate.

On the basis of transport phenomena, the kinetic model was developed describing bulk free radical polymerization of DAT. It predicts detailed reaction mechanism with degradative and effective chain transfer reactions already proposed by several authors using different analytical methods (NMR, FTIR)[8,27] and will be further on reffered to as *Detailed Kinetic Model* (DKM).

Several common and valid assumptions were made in order to simplify the kinetic model to some extent for both cases: (i.) no impurities are present in the reaction mixture; (ii.) polymerization is homogeneous; (iii.) the initiator decomposition occurs only by thermal methods; (iv.) thermal initiation of DAT is negligible as it appears only at very high temperatures over 170 °C[27]; (v.) no intramolecular cyclization occurs in polymerization of DAT due to steric hindrances of allyl groups.[27]

The proposed reaction pathway as the basis for kinetic mechanism is shown in Figure 1, where I_2 is the initiator, $I^\bullet$, are the initiator radicals, M is the monomer, $R_i^\bullet$ are live polymer radicals.

From the proposed reaction pathway the kinetic mechanism in the DKM was described as follows

$I_2 \rightarrow 2I^\bullet$ *initiator decomposition*

$I^\bullet + \mathrm{DAT} \rightarrow R^\bullet$ *initiation of monomer*

$R_{i-1}^\bullet + \mathrm{DAT} \rightarrow R_i^\bullet$ *propagation*

$R_{i-1}^\bullet + \mathrm{DAT} \rightarrow R_{i-1} - \mathrm{H} + \mathrm{RS}^\bullet \Leftrightarrow {}^\bullet\mathrm{RS}$
degradative chain transfer

$R_i^\bullet + \mathrm{DAT} \rightarrow R_{i+1/2\mathrm{DAT}} + \mathrm{R} - \mathrm{COO}^\bullet$
effective chain transfer

$R_i^\bullet + R_j^\bullet \rightarrow D_i + D_j$ *termination*

However, several assumptions had to be made to simplify the reaction scheme: (i.) reinitiation of resonance-stabilized radicals ($R_{RS}^\bullet$), which occurs during degradative chain transfer, is negligible,[29] (ii.) DAT does not cyclize intramolecularly,[8] (iii.) polymerization rates of cyclic intermolecular and non-intermolecular cyclic radicals are the same.[27] The dissociation of the initiator is presented as the first order reaction and can be written as:

$$r_{I_2} = k_d[I_2] \tag{1}$$

where k_d is the initiator decomposition rate coefficient.

It is generally accepted that quasy steady state assumption (QSSA) can be applied to the initiator radicals ($I^\bullet$) formed by the decomposition of the initiator. Assuming that the rate of the initiator dissociation is the rate limiting step, the rate of initiation may be simplified as

$$r_i = 2\eta_I k_d[I_2] \tag{2}$$

The propagation rate equation can be written as

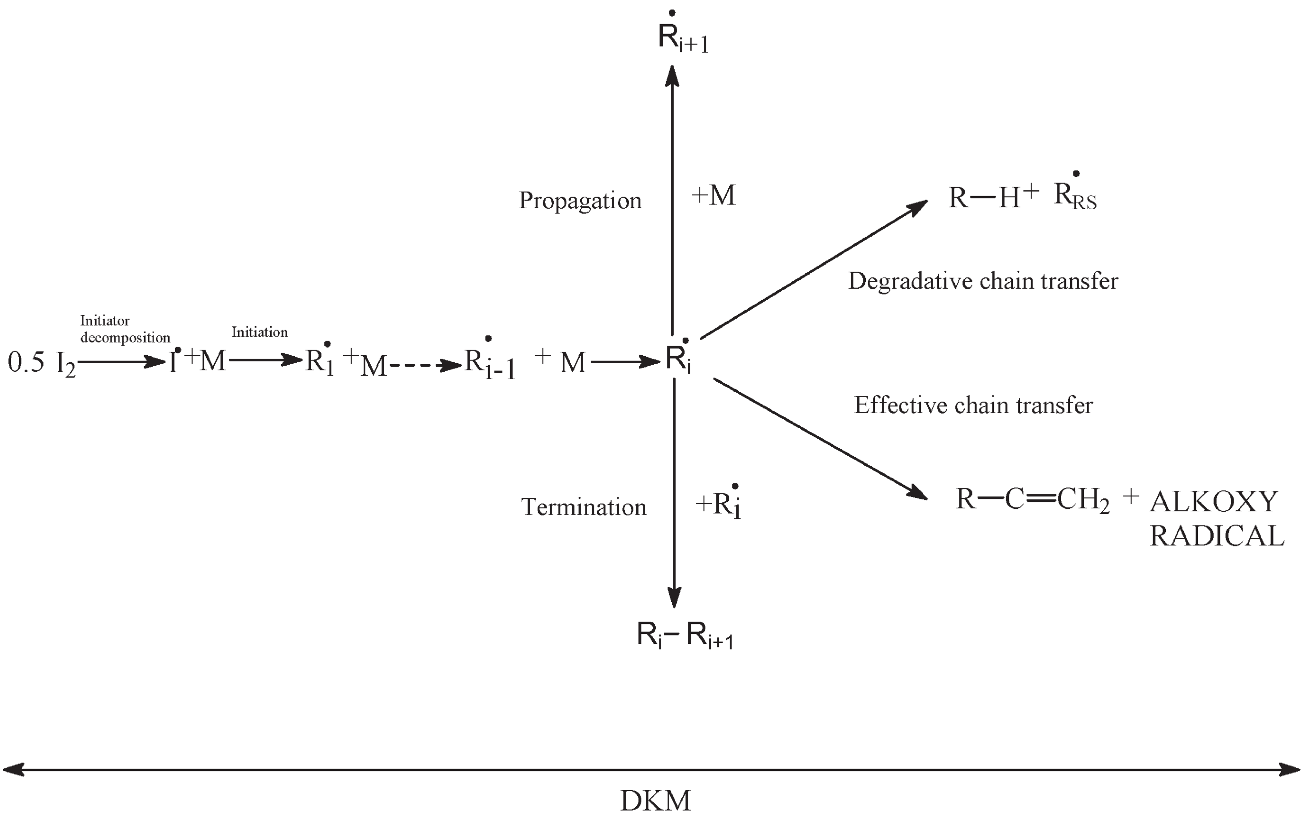

Fig. 1 – *Reaction pathway*

$$r_p = k_p\,[M]\,[R^\bullet] \qquad (3)$$

and the termination rate as

$$r_t = k_t\,[R^\bullet]\,[R^\bullet] \qquad (4)$$

Finally, degenerative and effective chain transfer reactions are summarized in the following kinetic expression

$$r_{\mathrm{Ch.Tr.}} = k_{\mathrm{Deg}}\,[M]\,[R^\bullet] + k_{\mathrm{Eff}}\,[M]\,[R^\bullet] \qquad (5)$$

The most direct method for solving the set of the species balances is to numerically integrate the differential mass balance equations derived directly from the kinetic equations. One has to postulate that the polymer chain does not grow beyond a certain number of monomer units in order to reduce the problem into a finite set of differential equations.[28] The second method is to construct a set of ordinary differential equations (ODEs) based on statistical moments of molecular weights. The methods of moments gives some valuable and accurate informations from a reduced set of equations and much simplified mathematics. It is perhaps the most widely used method in modeling of polymerization reactions. The idea is to combine the infinite set of unknowns into a family of polynomials called the moments of the generating function. For the calculation of molar mass, the following molar mass moments are defined for live and dead polymers

$$\lambda_k = \sum_{i=1}^{\infty} i^k\,[R^\bullet] \qquad (6)$$

and

$$\mu_k = \sum_{i=1}^{\infty} i^k\,[R^\bullet] \qquad (7)$$

where λ_k and μ_k denote the k-th moment of live and dead polymers, respectively. It follows that λ_0 is the total radical concentration of dead polymers and μ_0 is the total concentration of dead polymers, while $\lambda_1 + \mu_1$ is the concentration of monomer which has reacted.

The number average polymer molar mass are as follows

$$\overline{M_n} = M_M \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} \qquad (8)$$

The model equations were derived and are

$$\frac{d[I_2]}{dt} = -k_d[I_2] \qquad (9)$$

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = -(k_\mathrm{P} + k_\mathrm{Deg} + k_\mathrm{Eff})[\mathrm{M}]\lambda_0 \qquad (10)$$

$$\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = 2\eta_\mathrm{I} k_\mathrm{d}[\mathrm{I}_2] - k_\mathrm{Deg}[\mathrm{M}]\lambda_0 - k_\mathrm{t}\lambda_0^2 \qquad (11)$$

$$\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = 2\eta_\mathrm{I} k_\mathrm{d}[\mathrm{I}_2] - (k_\mathrm{Deg} + k_\mathrm{Eff})[\mathrm{M}]\lambda_1 - \\ - k_\mathrm{t}\lambda_0\lambda_1 + k_\mathrm{p}[\mathrm{M}]\lambda_0 \qquad (12)$$

$$\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = 2\eta_\mathrm{I} k_\mathrm{d}[\mathrm{I}_2][\mathrm{M}] - (k_\mathrm{Deg} + k_\mathrm{Eff})[\mathrm{M}]\lambda_2 - \\ - k_\mathrm{t}\lambda_0\lambda_2 + k_\mathrm{p}[\mathrm{M}](\lambda_0 + 2\lambda_1) \qquad (13)$$

$$\frac{\mathrm{d}\mu_0}{\mathrm{d}t} = (k_\mathrm{Deg} + k_\mathrm{Eff})[\mathrm{M}]\lambda_0 + k_\mathrm{t}\lambda_0^2 \qquad (14)$$

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}t} = (k_\mathrm{Eff} + k_\mathrm{Deg})\lambda_1[\mathrm{M}] + k_\mathrm{Deg}\lambda_0[\mathrm{M}] + k_\mathrm{t}\lambda_0\lambda_1 \qquad (15)$$

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}t} = (k_\mathrm{Eff} + k_\mathrm{Deg})\lambda_2[\mathrm{M}] + k_\mathrm{Deg}\lambda_0[\mathrm{M}] + k_\mathrm{t}\lambda_0\lambda_2 \qquad (16)$$

To estimate the kinetic rate coefficients values through the entire course of the reaction an algorithm developed by *Chiu* et al.[16] was used. Rate coefficients depend on temperature, chain mobility of radicals (hence diffusion), and on the viscosity of the reaction medium.[19,21] All those considerations must be incorporated into the mathematical description, underlying the calculation of the kinetic rate coefficients.

Theories of diffusion controlled reactions, with regard to the encounter pair model, were discussed and reviewed in detail elsewhere.[30-32] Both the rates of propagation and termination are subject of diffusion control due to the limited mobility of the long chain radicals caused by sudden viscosity increase and chain entanglements. The CCS model,[16] however, proposes that the effective kinetic constants are the sum of the inverse of chemical constant and that of a diffusion constant and are in form of

$$\frac{1}{k_\mathrm{p}} = \frac{1}{k_\mathrm{p0}} + \frac{1}{k_\mathrm{p,d}} \qquad (17)$$

$$\frac{1}{k_\mathrm{t}} = \frac{1}{k_\mathrm{t0}} + \frac{1}{k_\mathrm{t,d}} \qquad (18)$$

for propagation and termination, respectively.

The diffusion – controlled constants were defined as

$$k_\mathrm{p,d} = \Theta_\mathrm{p} \cdot \frac{\lambda_0}{U} \qquad (19)$$

$$k_\mathrm{t,d} = \Theta_\mathrm{t} \cdot \frac{\lambda_0}{U} \qquad (20)$$

where

$$\Theta_\mathrm{p} = A_\mathrm{Qp} \cdot \exp\left(\frac{-E_\mathrm{Qp}}{RT}\right) \qquad (21)$$

$$\Theta_\mathrm{t} = A_\mathrm{Qt} \cdot [\mathrm{I}_2]\exp\left(\frac{-E_\mathrm{Qt}}{RT}\right) \qquad (22)$$

and

$$U = \exp\left(2.3 \cdot \frac{\phi_\mathrm{m}}{(A + B \cdot \phi_\mathrm{m})}\right) \qquad (23)$$

where k_p0 and k_t0 are the two intrinsic kinetic rate constants related to the diffusion nature in the polymerization system.[16]

Apparent propagation rate constant was used for determinating the degradative and the effective chain transfer rate constants by an already proposed approach of *Divakar* and *Rao*.[9] ν represents the number of monomer molecules which reacted with a polymer chain radical during polymerization. The degree of polymerization and kinetic chain length were used for determining the ratio of the degradative and the effective chain transfer constant to propagation one, respectively.

The intercept from the plot of $1/\nu$ against the r_p gives $k_\mathrm{Deg}/k_\mathrm{p}$ ratio[9]

$$\frac{1}{\nu} = \left(\frac{k_\mathrm{t} r_\mathrm{p}}{k_\mathrm{p}^2[\mathrm{M}]^2}\right) + \frac{k_\mathrm{Deg}}{k_\mathrm{p}} \qquad (24)$$

and the intercept of $1/\eta_\mathrm{DP}$ against the r_p gives $(k_\mathrm{Deg} + k_\mathrm{Eff})/k_\mathrm{p}$ ratio[9]

$$\frac{1}{\eta_\mathrm{DP}} = \left(\frac{k_\mathrm{r} r_\mathrm{p}}{k_\mathrm{p}^2[\mathrm{M}]^2}\right) + \left(\frac{k_\mathrm{Deg} + k_\mathrm{Eff}}{k_\mathrm{p}}\right) \qquad (25)$$

The rate constants of degradative and effective chain transfer are functions of the propagation rate constants, therefore they depend on the conversion.[9]

Initiator efficiency, η_I, was assumed as a constant through the entire reaction[20,34] due to complexity of the kinetic modeling. Computer simulations were run assuming isothermal behavior. The model equations derived above were simultaneously solved by the Rosenbrook method.

Results and discussion

In this section, the kinetic parameters obtained are represented and discussed in detail; model predictions are compared with experimentally measured data of conversions for isothermal batch diallyl terephtalate polymerization at different reaction temperatures and various initiator loadings.

Figure 2 shows the FTIR spectra of DAT and peroxide initiator at different polymerization times. The absorption band at 1648 cm^{-1} is characteristic for the allylic C=C bond vibrations of DAT which corresponds with the monomer conversion. The bands at 1576 cm^{-1} and 1609 cm^{-1} represent first and second benzene ring vibrations and do not change during the polymerization. On this basis, the area under those peaks was taken as the internal standard during measurements and was used for the calculation of normalized absorbancy intensities at different times. From normalized values of peak areas the conversions were calculated with the use of relation[35-38]

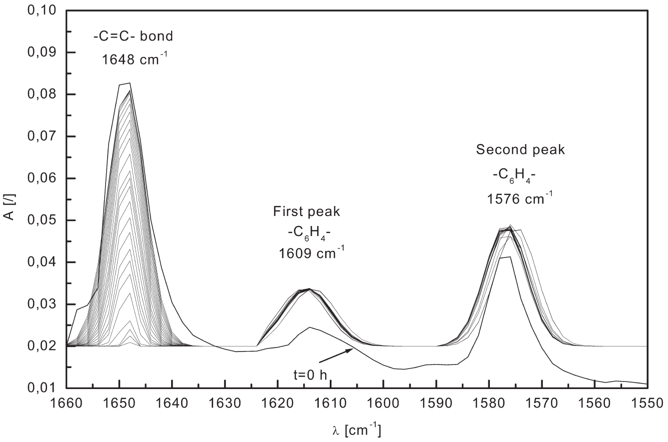

Fig. 2 – *Deconvolution of FTIR spectra for w = 5 % initiator dicumyl peroxide, 120 °C for different reaction times*

$$\chi = 1 - \frac{S_{1648}^{t} \Big/ S_{\text{benzene ring}}^{t}}{S_{1648}^{t=0} \Big/ S_{\text{benzene ring}}^{t=0}} \tag{26}$$

where $S_{1648}^{t}/S_{1648}^{t=0}$ are the areas of the 1648 cm^{-1} peaks at time t and $t = 0$, respectively, and $S_{\text{benzene ring}}^{t}/S_{\text{benzene ring}}^{t=0}$, are the areas of the benzene peaks at time t and time $t = 0$, respectively.

k_d rate coefficients for this initiator monomer system were evaluated with the use of dead end theory.[17,18] When fast initiators in small initial loadings are used, the polymerization stops at quite low conversions due to high diffusion limitations, which may be termed as *the dead end polymerization*.[17,18] k_d rate coefficients depend on the viscosity of the reaction medium and on the temperature.[39] For their exact determination next assumptions should be made: (a.) a simple kinetic mechanism composed of initiation, propagation and two modes of termination was proposed,[17,18] (b.) the initiator decomposition is the first order rate equation independent from the initiator concentration and the rate limiting step,[17,18] (c.) the QSSA.[17,18]

From those assumptions the final form of equation was obtained, where the only fit quantity is k_d

$$\ln\left[1 - \frac{\ln(1-\chi)}{\ln(1-\chi_\infty)}\right] = -\frac{k_d t}{2} \tag{27}$$

where χ and χ_∞ are the conversions at time t and $t = \infty$.

Experimentally obtained kinetic quantities of k_d for these systems were compared with those reported in literature[39-41] and a good agreement was obtained (Table 1). The differences were attributed to a different initiator monomer system and to different viscosity of the reaction medium.[42] The evaluated initiator decomposition rate coefficients were used for model calculations.

Table 1 – *Comparison between the measured and literature reported initiator decomposition rate coefficients, obtained for w=0.1 to 0.8 % of initiators*

	$E_{\text{d exp.}}$ kJ mol^{-1}	$E_{\text{d ref.}}$ kJ mol^{-1}	$A_{\text{d exp.}}$ s^{-1}	$A_{\text{d ref.}}$ s^{-1}
CHPC	(125.1 ± 5.57)	112 [39]	$(1.2 \pm 0.84) \cdot 10^{15}$	$3.78 \cdot 10^{13}$ [39]
DCPO	(90.2 ± 5.4)	120 [37,40]	$(1.2 \pm 0.50) \cdot 10^{8}$	$8.40 \cdot 10^{11}$ [37, 40]

The effect of temperature on polymerization reaction was estimated. The results are similar to those reported in other systems (MMA and PS).[6a,6b] Higher monomer conversions were obtained at higher reaction temperatures, but only to a certain degrees, at higher ones the behavior was quite the opposite. The final conversion starts decreasing with further increase of the reaction temperature. At very high temperatures, the initiator concentration drops immediately, therefore the polymerization rate falls of, the diffusion limitations increase and the reaction stops, resulting in a lower final conversion. The same effect is observed at high conversions, where an increase in viscosity is observed, which diminishes the mobility of polymer chains, therefore, propagation and termination rates become diffusion-controlled and their values decrease seriously, especially after gel point (GP), when the viscosity of the reaction medium strongly increases.[16,19] The same observations were made by the use of other initiator types and other monomer systems.[6a,6b,19]

The calculated apparent k_p and k_t rate constants as a function of conversion at different temperatures and different types of initiators are shown in Figure 3.

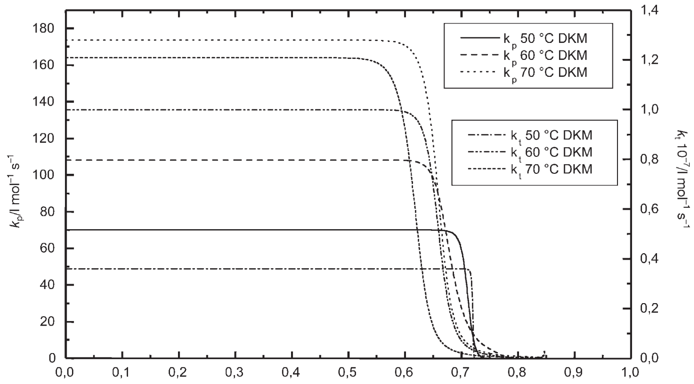

Fig. 3a – *Apparent k_p and k_t rate constants for w = 5 % of dicyclohexyl peroxydicarbonate initiator load-*

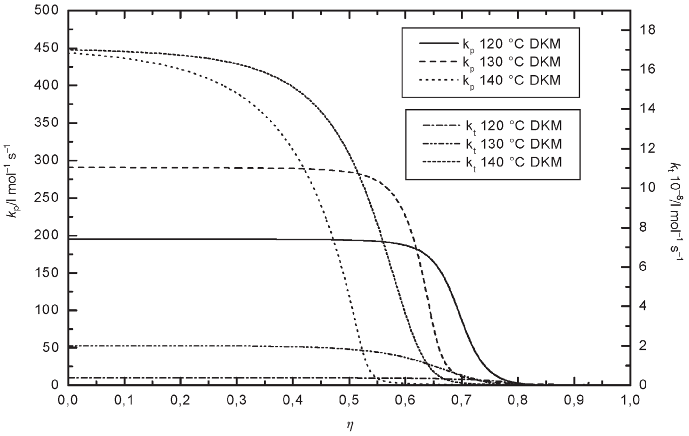

Fig. 3b – *Apparent k_p and k_t rate coefficients for w = 5 % of dicumyl peroxyde initiator loadings*

It is obvious that similar behavior for k_p and k_t with an initial plateau at low conversions was predicted. The plateau duration depends on the reaction temperature as well as on the type of the initiator. However, it has been observed that the influence of the initiator loading is negligible in the drop off of the propagation rate coefficients, because Θ_P is independent from the initiator concentration eq. (21). The same tendency was obtained in other bulk polymerization systems (MMA-PMMA and St-PS) in thermally and photochemically initiated polymerization.[16,19,43]

Activation energies and preexponential factors of intrinsic propagation and termination rate constants for kinetic model were obtained from an Arrhenius plot of ln k_{p0} and ln k_{t0} versus $1/T$, respectively, and are shown in Table 2. Unfortunately, no reports for their comparison were found in literature.

Table 2 – *Kinetic parameters*

$k_{p0} = A_p \exp(-E_p/RT)$		$k_{t0} = A_t \exp(-E_t/RT)$	
A_p/l mol^{-1} s^{-1}	E_p/kJ mol^{-1}	A_t/l mol^{-1} s^{-1}	E_t/kJ mol^{-1}
$(3.6 \pm 0.9) \cdot 10^7$	(36.9 ± 1.8)	$(1.7 \pm 0.01) \cdot 10^{28}$	(144.7 ± 20.2)
$1/\Theta_p = A_{Qp} \cdot \exp(-E_{Qp}/RT)$		$1/\Theta_t = A_{Qt} \cdot \exp(-E_{Qt}/RT)$	
A_{Qp}/s^{-1}	E_{Qp}/kJ mol^{-1}	A_{Qt}/s^{-1}	E_{Qt}/kJ mol^{-1}
$(5.60 \pm 0.04) \cdot 10^{80}$	(651.0 ± 74.0)	$(7.48 \pm 0.03) \cdot 10^{31}$	(777.9 ± 2.4)

Before the GP, k_{p0}, k_{t0} and η_I, as the only adjustable model parameters, were obtained by fitting the kinetic rate equations onto experimentally measured data. Above the GP, four addition temperature dependent parameters A, B, Θ_p and Θ_t needed to be evaluated. In estimating the values of the parameters from the experimental data an important step is the right choice of initial values due to the fact, that the higher the number of adjustable parameters, the larger the autocorrelation among them.[6a,6b]

The dependence of model parameters on the various operating variables of the polymerization process, i.e. initiator loading $[I_2]$ and the temperature of reaction T, was estimated. According to eqs. (21) and (22) the temperature dependence of $[1/\Theta_t]$ and $1/\Theta_p$ reflects primarily on the behavior of diffusion coefficient (D) in termination and propagation rate coefficients, respectively.[26] From the slopes of the curves ln $1/\Theta_p$ and ln Θ_t versus $1/T$ the activation energy of the mass transport processes for growing radicals and monomers for DKM were determined (Table 2). From the kinetic modeling at the different initiator loadings it was observed that values of Θ_p remain constant, depending only on the reaction temperature, while Θ_t decreases with an increase of the initiator concentration, which is in agreement with the results reported elsewhere.[16,19] It has to be noted, that Θ_t is consistently greater at lower initiator loading, presumably due to a weak dependence of D on molar mass. Lower initiator loading results in higher molar mass of polymers, which decreases D. The same tendency was observed for other initiator monomer systems.[6a,6b,16,19]

The remaining two kinetic parameters A and B were examined to find that they both increase with temperature, and are shown in Table 3. However, due to a very high sensitivity of kinetic model on these two parameters, it is difficult to determine their exact temperature dependence. Similar tendency was observed in the work of *Fujita* et al.[33]

The ratios of the degradative and the effective chain transfer to propagation rate constants were estimated from average molar mass of the samples

Table 3 – *Kinetic parameters for DKM*

Initiator type	$f = F + f \cdot T$		$E = E + e \cdot T$		$A = A + a \cdot T$	
	$F \cdot 10$	$f \cdot 10^3$	E	e	$A \cdot 10$	$a \cdot 10^4$
CHPC	(58.4 ± 0.5)	(–15.9 ± 0.2)	(51.7 ± 8.0)	(–0.14 ± 0.04)	(–0.055 ± 0.008)	(0.45 ± 0.25)
DCPO	(49.0 ± 12.1)	(–11.6 ± 3.1)	(69.5 ± 2.4)	(–0.16 ± 0.06)	(–3.9 ± 0.9)	(12.1 ± 2.6)

Initiator type	$B = B + b \cdot T$		$H(T) = H + h \cdot T$		$G([I_2]) = G + g \cdot \ln[I_2]$	
	$B \cdot 10$	$b \cdot 10^4$	$H \cdot 10^2$	$h \cdot 10^3$	G	g
CHPC	(–0.16 ± 0.03)	(0.95 ± 0.09)	(–31.0 ± 9.6)	(1.0 ± 0.3)	(0.62 ± 0.1)	(–0.43 ± 0.06)
DCPO	(–11.3 ± 1.2)	(30.0 ± 3.1)	(–45.0 ± 0.84)	(1.2 ± 0.02)	(0.87 ± 0.1)	(–0.27 ± 0.09)

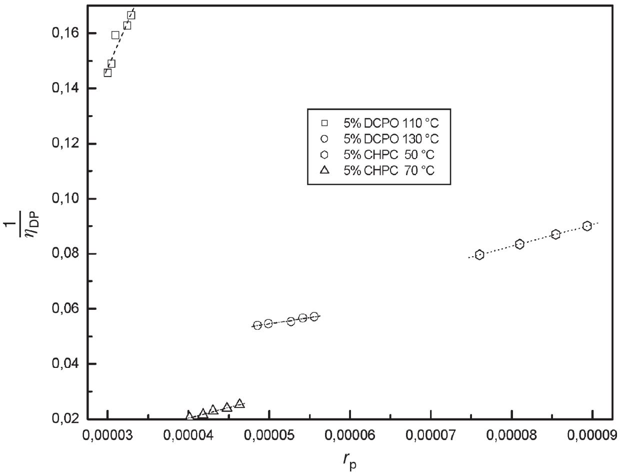

Fig. 4 – *Determination of* $(k_{Deg} + k_{Eff})/k_p$ *ratio for dicumyl peroxide and dicyclohexyl peroxydicarbonate initiators*

what is shown in Figure 4, for CHPC initiator. Ratios of k_{Deg}/k_p and k_{Eff}/k_p were obtained from intersection of $1/\eta_{DP}$ *versus* $r_p/[M]^2$. Ratios of k_{Deg}/k_p were in the range between 0.01 to 0.06 and ratios of k_{Eff}/k_p in the range between 0.001 to 0.008, what is in a good agreement to results obtained in study of *Divakar* and *Rao*,[9] for DAP polymerization. In addition, both ratios increase with temperature, therefore, it was estimated that at higher temperatures the degradative and the effective chain transfers are favored with regard to the propagation reactions. The k_{Deg} and k_{Eff} rate coefficients depend on the type of the initiator, initiator loading and the reaction temperature.[9]

The comparison of model predicted conversions and experimentally measured ones for various initiator types are shown in Figure 5. It was observed that DKM successfully predict measured conversions. Tables 2 and 3 summarize the model parameters used for kinetic model fitting.

The parity plot for various initiator types is shown in Figure 6. It represents the difference among calculated conversions from both models and experimentally measured ones. As can be seen, the majority of the data are found within ± 10 % error band. The number of points lying outside the error band increases as the reaction temperature rises. At higher

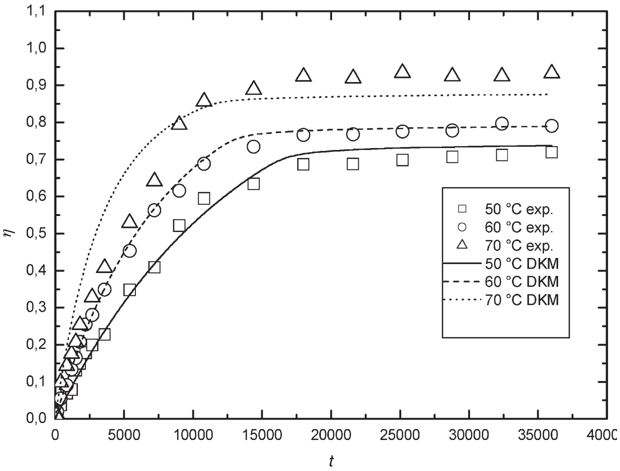

Fig. 5a – *Comparison of DKM and experiment for w = 5 % of dicyclohexyl peroxydicarbonate*

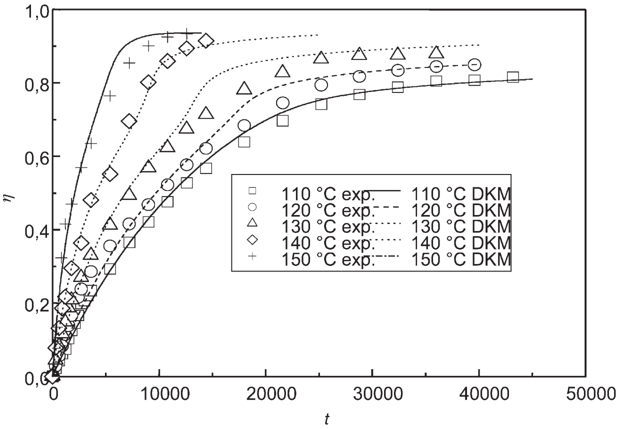

Fig. 5b – *Comparison of DKM and experiment for w = 5 % of dicumyl peroxyde*

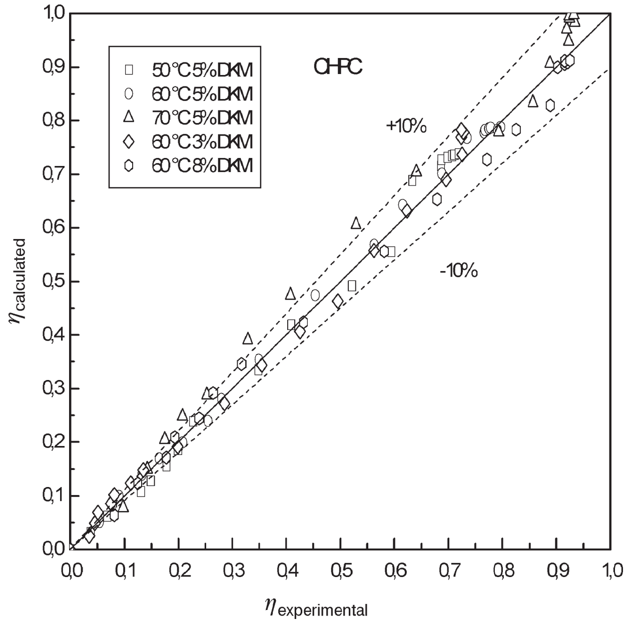

Fig. 6a – *Parity plot of DKM for various initiator loadings of dicyclohexyl peroxydicarbonate*

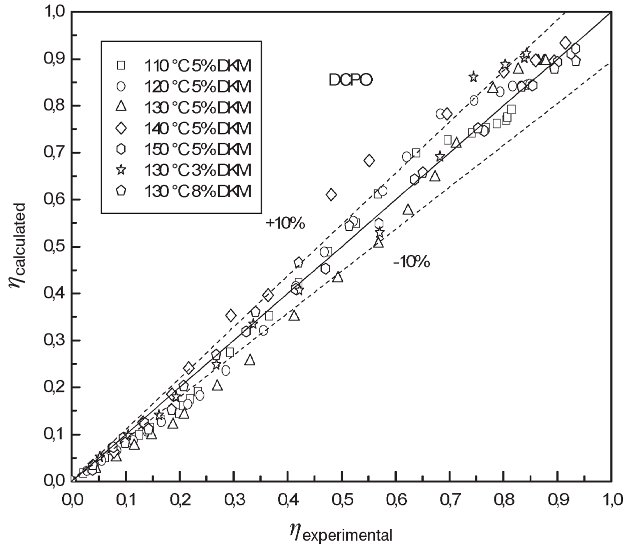

Fig. 6b – *Parity plot of DKM for various initiator loadings of dicumyl peroxyde*

temperatures, especially at the final stage of polymerization, more points are located outside the error band.

The average molar mass may also be calculated from the solution of kinetic model by using optimized kinetic parameters, reported in Table 2 and 3. The results up to gel point are shown in Figure 7. In general, a good agreement between predicted and experimentally calculated number of average molar mass was obtained. The calculated polydispersities for different initiator types and temperatures varied between 1.92 and 2.2 in all runs. Unfortunately, no data were found in the available literature for their comparison.

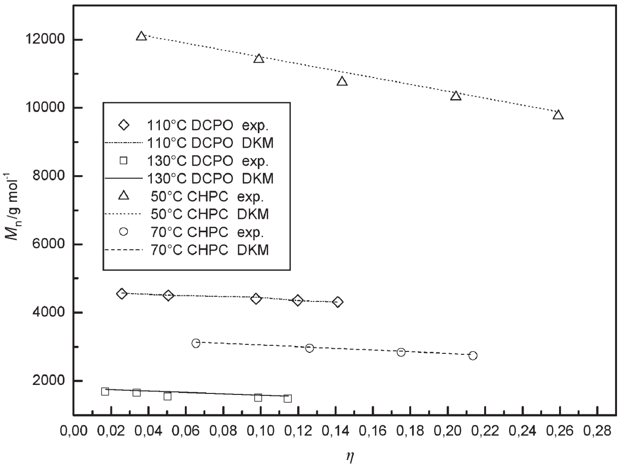

Fig. 7 – *Number of average molar mass up to gel point for w = 5 % of various initiators at various temperatures*

Conclusions

Based on the study of the bulk diallylterephthalate polymerization, the following conclusions were made:

The activation energies of kinetic rate coefficients for propagation were estimated. Their values were 36.9 kJ mol^{-1} for propagation and 144.7 kJ mol^{-1} for termination. The propagation activation energy is in good agreement to result obtained from DSC study (32 kJ mol^{-1}) for diallyl orthophthalate.[36] Unfortunately, no reports for termination activation energy for diallyl phthalates can be found in the literature.

Free radical polymerization in bulk phase can be satisfactorily described by DKM developed kinetic model, which includes three main reactions directions, the initiation, propagation and termination. In addition, it incorporates two reaction directions the degradative and the effective chain transfers, which are characteristic for allyl polymerizations. The developed kinetic model may be of use for engineering purposes.

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Nomenclature

η_I – initiator efficiency, –
k_{p0} – intrinsic propagation rate coefficient, l mol^{-1} s^{-1}
k_{t0} – intrinsic termination rate coefficient, l mol^{-1} s^{-1}
k_p – apparent propagation rate coefficient, l mol^{-1} s^{-1}
k_t – apparent termination rate coefficient, l mol^{-1} s^{-1}

Θ_p – characteristic monomer diffusion time constant, s^{-1}
Θ_t – characteristic migration time constant of growing radicals, s^{-1}
λ_i – i-th moment of the growing live radical distribution, mol l^{-1}
μ_i – i-th moment of the dead radical distribution, mol l^{-1}
ϕ_m, ϕ_p – volume fraction of the monomer and the polymer, –
E_p, E_t – activation energies of propagation and termination, J mol^{-1}
E_{Qp}, E_{Qt} – activation energies of Θ_p and Θ_t, J mol^{-1}
$[I_2]$ – concentration of the initiator, mol l^{-1}
$[I\bullet]$ – concentration of the initiator radicals, mol l^{-1}
$[M]$ – concentration of the monomer, mol l^{-1}
$[D_i]$ – concentration of the dead polymers, mol l^{-1}
$[R_i\bullet]$ – concentration of the radicals, mol l^{-1}
T – temperature, K
ν – kinetic chain length, –
η_{DP} – degree of polymerization, –
$\overline{M}_n$ – number of average molar mass of the polymer, g mol^{-1}
M_M – molar mass of monomer, g mol^{-1}
R – universal gas constant, J mol^{-1} K^{-1}
k_{Deg} – degradative chain transfer rate coefficient, l mol^{-1} s^{-1}
k_{Eff} – effective chain transfer rate coefficient, l mol^{-1} s^{-1}
t – time, s
k_d – initiator decomposition rate constant, s^{-1}
r_p, r_t – propagation rate and termination rate, mol l^{-1} s^{-1}, s^{-1}
χ, χ_∞ – conversion of DAT, –
A_p, A_t – Arrhenius frequency factor of propagation and termination rate constant, l mol^{-1} s^{-1}
A_{Qp}, A_{Qt} – Arrhenius frequency factor of Θ_p and Θ_t, s^{-1}
$H = \dfrac{k_{Deg}}{k_p}$ – the ratio of degradative chain transfer to propagation rate constant, –
$G = \dfrac{k_{Deg} + k_{Eff}}{k_p}$ – the ratio of degradative and effective chain transfer to propagation rate constant, –
H_i, h_i, G_i, g_i, A_i, a_i, B_i, b_i, F_i, f_i, E_i, e_i – individual kinetic parameters, –
w – mass fraction, %

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