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Thermal properties of ester-amide copolymers with cyclic groups in oligoamide soft segment

RAPID COMMUNICATION

Summary — Thermoplastic poly(ester-*block*-amide) elastomers (PEAs) comprising hard blocks of oligoester [oligo(butylene terephthalate), PBT] and oligoamide soft segments [reaction product of 1,4-cyclohexanediamine (CHDA) with dimerized fatty acid (DFA)] were synthesized and analyzed by differential scanning calorimetry (DSC). The influence of segments content (w_s:w_h) and oligoamide block length (DP_s) on the glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) were examined. Increasing the soft segment molecular weight by reacting DFA with diamine resulted in a decreasing ability of forming a homogenous mixture with the amorphous PBT phase, thus, affecting elastomer properties. PEA containing cyclic group (from CHDA) in oligoamide soft segment exhibits higher temperature transitions contrary to PEA based on 1,6-hexamethylenediamine.

Keywords: poly(ester-*block*-amide), thermoplastic elastomers, soft oligoamide segments, phase transition temperatures, oligoamide cyclic groups.

Poly(ester-*block*-amide)s (PEAs) belong to a group of multiblock copolymers, so called thermoplastic elastomers, which consist of blocks with different properties (soft and hard segments). Oligourethane and oligourea residues, aromatic oligoesters and oligoamides were used as hard segments, whereas soft segments consisted of oligoethers, oligosiloxanes or dimerized fatty acids [1—7]. To obtain the material described above, soft and hard phases have to be immiscible [8, 9].

Poly(ester-*block*-amide)s investigated in the present work consisted of crystallized sequences of poly(butylene therephthalate) (PBT) as the hard segments and aliphatic, mostly amorphous, oligoamide sequences obtained from diamines and dimerized fatty acids (DFA) as the soft segments.

Pure DFA has been widely applied as soft segments in block copolymers [10, 11]. The relatively small DFA-molecule caused significant mutual miscibility of the soft and hard blocks, what considerably changes elastomer properties. The main idea of this work was to reduce mutual miscibility of soft and hard segments through increasing the soft segment molecular weight by reacting DFA with diamine. As expected, this reaction leads to a decrease in the glass-transition temperature and improvement of mechanical properties. The soft phase also contains non-crystalline PBT sequences [12, 13].

This paper describes the thermal properties of PEA in relation to the contents and molecular weights of the soft segments.

EXPERIMENTAL

Materials

Synthesis of poly(ester-*block*-amide)s were carried out using the commercially available substrates, namely: dimethyl terephthalate (DMT, Elana SA); 1,4-butanediol (1,4-BD, BASF); magnesium titanate catalyst; dimerized fatty acid (DFA) Pripol 1009 — product of dimerization of linoleic C_{18} acid — molecular weight ~570 g·mole^{-1} (Uniqemia Chemie, BV, Netherlands); 1,4-cyclohexanediamine (CHDA) (Aldrich Chemie, Steinhein).

Synthesis

Synthesis of poly(ester-*block*-amide)s was a three-step process: oligoamide preparation, transesterification and polycondensation in the melt.

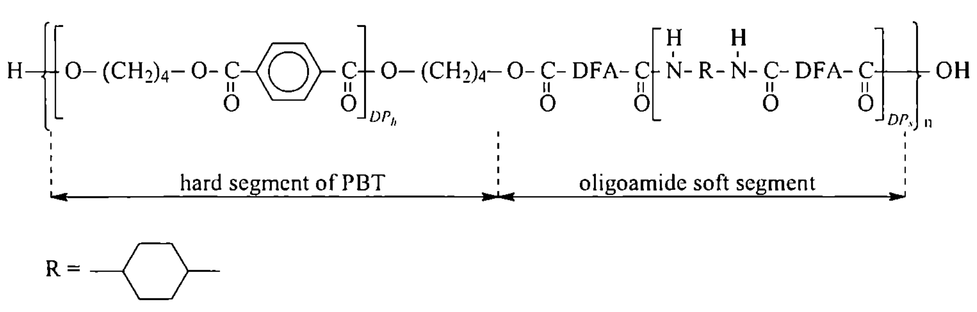
Transesterification of DMT and 1,4-BD in molar ratio 1:2 was the first step. The reaction was carried out in presence of magnesium titanate organometalic complex as catalyst. Oligoamide preparation from CHDA and DFA was the second step. Polycondensation reaction of these two previously prepared intermediate compounds comprised the third step [12, 13].

Measurements

DSC measurements (heating-cooling-heating cycle) were conducted in a Perkin-Elmer (DSC-2) instrument, at heating and cooling rate of 10°C/min. The DSC calibration (base line) was performed with indium (156°C) and *n*-heptane (-90.5°C).

RESULTS AND DISCUSSION

Composition of synthesized PEA (formula I) is presented in Table 1.



(I)

Table 1. Composition of PEA (calculated from feed ratio)

No	Soft segment content W_s, %	Hard segment content W_h, %	Degree of polymerization of the soft segment, DP_s	Degree of polymerization of the hard segment, DP_h
1	20	80	1	21.6
2	40	60	1	7.9
3*)	50	50	1	5.1
4	60	40	1	3.3
5	80	20	1	1.0
6*)	50	50	1	5.1
7	50	50	3	11.1
8	50	50	5	17.0
9	50	50	7	22.9
10*)	50	50	1	5.1
11	67	33	3	5.1
12	76	24	5	5.1
13	81	19	7	5.1

*) Samples 3, 6 and 10 are the same copolymers.

Three groups of poly(ester-*block*-amide)s were synthesized. In the first group, the degree of polymerization of oligoamide (DP_s) was changed 1—7 range. Concentration of soft oligoamide segments varied from 20 to 80 wt. % at constant degree of polymerization of soft segment DP_s = 1 (constant oligoamide length, samples 1—5). The second group (samples 6—9) was prepared in 1:1 weight ratio of hard and soft segments with variable soft segment length (DP_s = 1-7). The third group (samples 10—13) was also prepared with variable degree of polymerization of oligoamide and with variable concentration of hard and soft segments in the copolymer.

Results of DSC examinations of poly(ester-*block*-amide)s are presented in Figs. 1—6.

DSC heating and cooling scans for first group consisting of 20—80 wt. % soft segments were compared with pure oligoamide (dash curve — CHDA-1, Figs. 1 and 2). Reported results clearly show that synthesized PEA with constant oligoamide segment length exhibits only one low-temperature glass transition (T_{g1}) attributed to the soft segments and well-defined melting point of hard segments (T_{m2}), thus, pointing to existence of two-phase systems in the products. Generally, glass transition temperature decreased with increasing soft segments concentration. Decrease of oligoamide concentration to 20 wt. % results in the melting point of soft segments (T_{m1}) become undetectable in DSC (Fig. 1). This group of

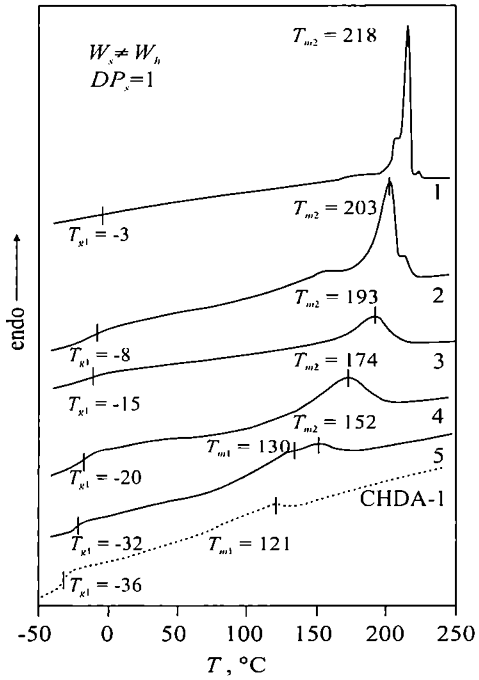


Fig. 1. Second heating DSC thermograms of samples 1—5; numbered curves refer to sample numbers in Table 1

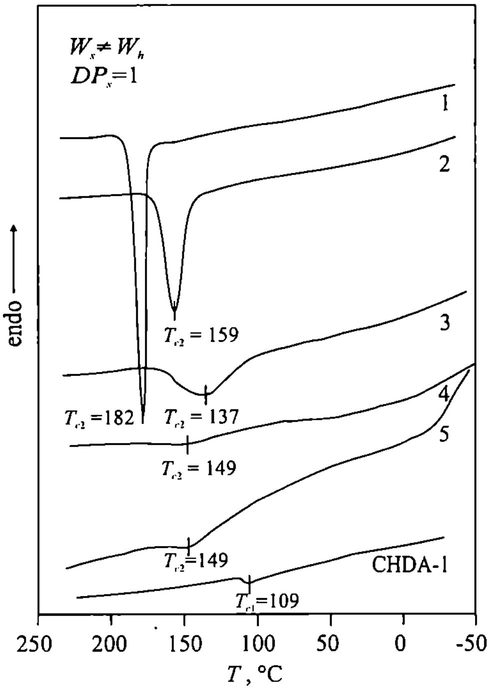


Fig. 2. Cooling DSC thermograms of samples 1—5; numbered curves refer to sample numbers in Table 1

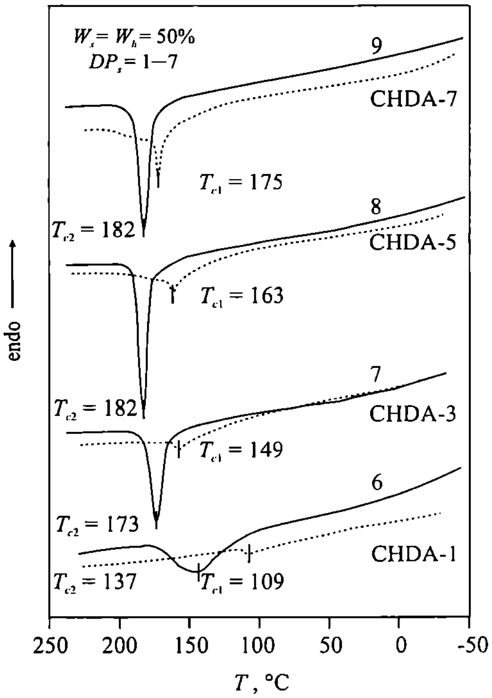


Fig. 4. Cooling DSC thermograms of samples 6—9; numbered curves refer to sample numbers in Table 1

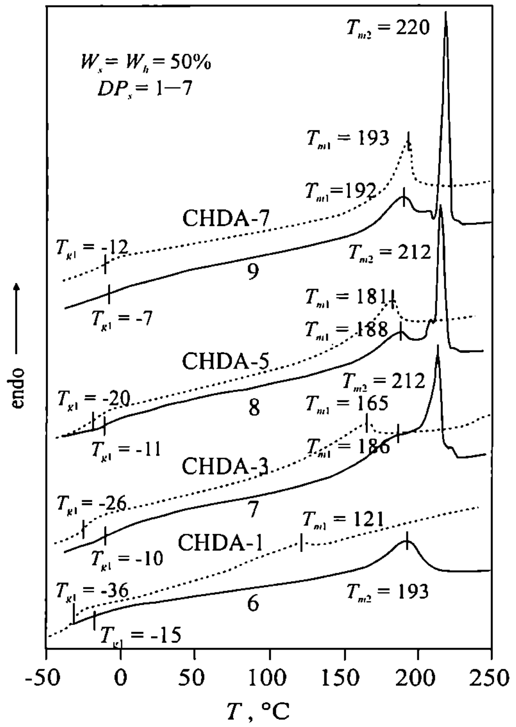


Fig. 3. Second heating DSC thermograms of samples 6—9; numbered curves refer to sample numbers in Table 1

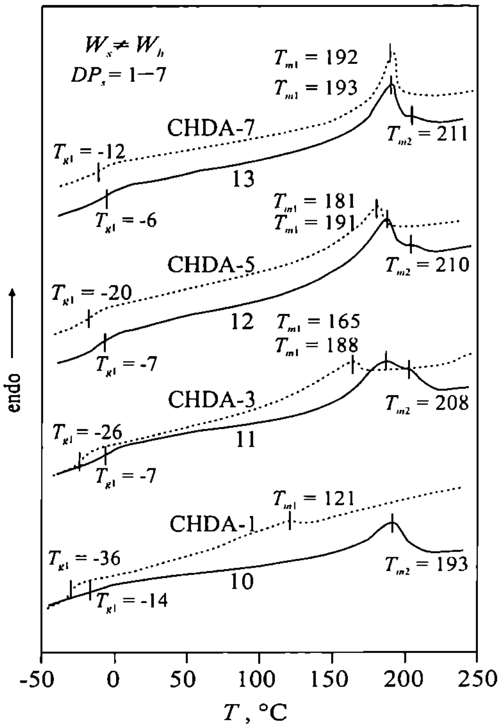


Fig. 5. Second heating DSC thermograms of samples 10—13; numbered curves refer to sample numbers in Table 1

PEA exhibits one crystallization temperature of PBT blocks (T_{c2}) (Fig. 2).

An interesting behavior can be observed for samples with different soft block lengths, namely CHDA-1 to CHDA-7 (dash curves), and their copolymers (full curves) (Figures 3—6). It can be concluded that pure oligoamide exhibits distinct endotherms ascribed to soft segment's melting (T_{m1}) and exotherms ascribed to crystallization temperatures (T_{c1}). Oligoamide melting and crystallization temperature increases with increasing degree of polymerization of the soft segments. High temperature transitions (T_{m2} and T_{c2}) are attributed to the melting and crystallization of PBT crystals.

Samples with 1:1 weight ratio exhibit two melting transition temperatures (Fig. 3), but only one crystallization transition is detectable (Fig. 4). Considering the very narrow spacing of the T_{m1} and T_{m2} melting endotherms, overlapping of both crystallization processes is the most probable explanation.

Two melting point maxima are visible for the group with variable segments content (samples 10—13), first — distinct for the oligoamide and second — small for the PBT (Fig. 5). This effect is connected with relatively small hard segment concentration in copolymer (Table 1). Contrary to results for two previous series, two crystallization temperatures were found (Fig. 6) which, by analogy, can be attributed to the soft (T_{c1}) and hard segment (T_{c2}) transitions, respectively.

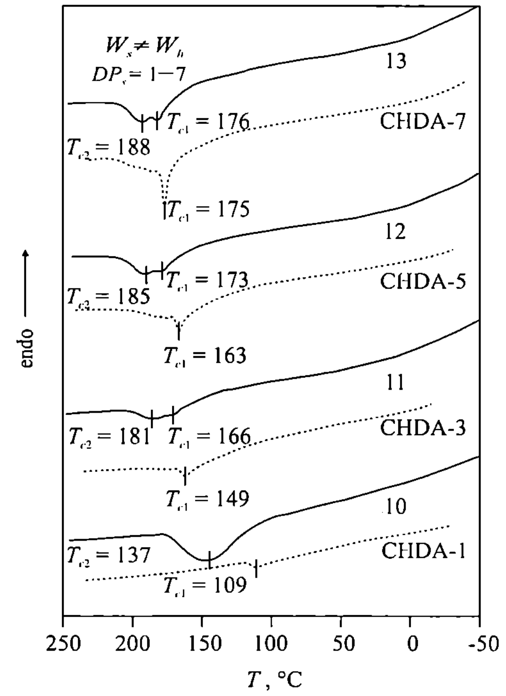


Fig. 6. Cooling DSC thermograms of samples 10—13; numbered curves refer to sample numbers in Table 1

This behavior suggests existence of differences in mutual miscibility of segments and indicates that increasing oligoamide segment length leads to microphase separation.

Relationship between the observed glass transition temperature and the molecular weight of soft segments is shown in Figs. 3 and 5. T_{g1} values increasing with oligoamide length could be due to the existence of hydrogen bonds from –NH– group between adjacent chains.

CONCLUSIONS

Poly(ester-*block*-amide) multiblock copolymers (PEAs) of definite composition show two melting and two crystallization transition temperatures, *i.e.* that of oligoamide in a lower-temperature region (the soft segment) and of the PBT sequences in the hard phase. Temperature transitions, especially T_{m1} and T_{m2}, of the soft oligoamide segment in PEA based on 1,4-cyclohexanediamine exhibit higher values as compared with those for PEA based on 1,6-hexametylenediamine [12, 13] (Table 2).

Table 2. Transition temperatures of pure oligoamides based on 1,6-hexametylene diamine and 1,4-cyclohexanediamine

DP_s	1,6-hexametylene diamine			1,4-cyclohexanediamine		
	T_{g1}, °C	T_{m1}, °C	T_{c1}, °C	T_{g1}, °C	T_{m1}, °C	T_{c1}, °C
1	-36	48	15	-36	121	109
3	-25	66	23	-26	165	149
5	-23	71	31	-20	181	163
7	-13	81	43	-12	192	175

Increasing oligoamide segment length decreases the ability to form a homogeneous mixture with the amorphous PBT phase. Described effects disadvantageously affect elasticity of copolymers.

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Rate coefficients as a function of time during the after-effect of a photoinduced crosslinking polymerization

RAPID COMMUNICATION

Summary — The polymerization of a dimethacrylate monomer occurring in the dark after the initiating light has been switched off (so-called after-effect) was modeled by assuming of two different termination mechanisms: monomolecular (Model 1) and bimolecular (Model 2). Time dependent monomolecular termination (k_t^m) and bimolecular termination (k_t^b) rate coefficients and a time independent propagation rate coefficient k_p are used in the models. Both k_t^m and k_t^b are polynomial functions of time. A very important feature of the newly developed models is that free terms of polynomials correspond to values of k_t^m (Model 1) or $k_p[P^\cdot]_0$ (Model 2) at the moment of stopping the irradiation (t_{dark} = 0; $[P^\cdot]_0$ constitute macroradical concentrations at t_{dark} = 0). Those values can be considered as describing the process during continuous irradiation. Calculations were performed for eight photoinduced polymerization processes, in which initiation had been interrupted at various degrees of double bond conversions (denoted as starting conversions). It was found that the conversion dependence of $k_t^b[P^\cdot]_0$ and k_t^m parameters extrapolated to t_{dark} = 0 appearing in two various termination models was similar.

Key words: photopolymerization, after-effect, (tetraethylene glycol) dimethacrylate, modeling, termination mechanism, time-dependent rate coefficients.

Photopolymerization of multifunctional monomers occurs with a marked postcuring effect. When light is cut off, the photoinduced reaction continues to proceed up to a significant conversion. This phenomenon, named the after-effect (or postpolymerization — post-effect), has found application in many industrial processes (*e.g.* in production of protective coatings for optical fibers). The after-effect is used also for determination of propagation and termination rate coefficients [1].

Termination reaction during the polymerization of multifunctional monomers can occur according to two possible mechanisms:

— monomolecular (radical trapping)

$$P_i^\cdot \xrightarrow{k_t^m} (P_i^\cdot)_{trapped} \tag{1}$$

where: $P^\cdot$ — *macroradical*, k_t^m — *monomolecular termination rate coefficient;*

and/or

— bimolecular (reaction between two macroradicals)

$$P_i^\cdot + P_i^\cdot \xrightarrow{k_t^b} \text{Polymer} \tag{2}$$

where: k_t^b — *bimolecular termination rate coefficient.*

It is generally accepted that during continuous initiation the bimolecular termination rate coefficient decreases as the polymerization proceeds, passing through a plateau [1]. However, radical trapping, and consequently monomolecular rate coefficient, should increase with double bond conversion [1—4].

Termination rate (R_t) during the after-effect, occurring in the absence of initiation, can be described by two mathematical models, assuming:

— monomolecular termination (Model I)

$$R_t^m = -\frac{d[P^\cdot]}{dt} = k_t^m \cdot [P^\cdot] \tag{3}$$

where: $[P^\cdot]$ — *radical concentration,*

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— bimolecular termination (Model II)

$$R_t^b = -\frac{d[P^\cdot]}{dt} = 2 \cdot k_t^b \cdot [P^\cdot]^2 \qquad (4)$$

These models together with the expression for the polymerization rate (R_p):

$$R_p = -\frac{d[M]}{dt} = k_p \cdot [M] \cdot [P^\cdot] \qquad (5)$$

where: [M] — *concentration of double bonds*, k_p — *propagation rate coefficient*
can be solved analytically giving expressions linking together the degree of double bond conversion in the dark with the time of dark reaction [5].

These obtained models are characterized by time-independent parameters: k_t^m, $k_t^b[P^\cdot]_0$ and $k_p[P^\cdot]_0$, where subscript refers to macroradical concentration at beginning of the dark period [5]. In our previous papers, where modeling was based on fitting these kinetic models to succeeding or increasingly longer time intervals of the dark reaction, we showed that values of the discussed parameters change as the reaction in the dark proceeds [2, 3].

In this work we attempted to describe kinetics of the after-effect by models assuming the first and second order termination mechanisms, but expressing the parameters k_t^m and $k_t^b[P^\cdot]_0$ as function of time.

MODELLING

Assuming that termination can proceed by the monomolecular or bimolecular mechanism, two new models describing polymerization during the after-effect were developed:

— Model 1

$$R_t^m = k_t^m(t) \cdot [P^\cdot] \qquad (6)$$

$$k_t^m(t) = \sum_{i=0}^{3} a_i t^i \qquad (7)$$

— Model 2

$$R_t^b = 2 \cdot k_t^b(t) \cdot [P^\cdot]^2 \qquad (8)$$

$$k_t^b(t) = \sum_{j=0}^{9} b_j t^j \qquad (9)$$

where: t — *time of the dark reaction* (t_{dark}).

It was assumed in these models that propagation rate coefficients k_p do not change with the reaction time, thus the polymerization rate in the both models is expressed by equation (5). Termination rate coefficients k_t^m and k_t^b are polynomial functions of time. Order of the polynomials describing dependence of termination rate coefficients on time of the dark reaction was found from the best fitting of the models to experimental data. Parameters a_0 and b_0, which correspond to the rate coefficients k_t^m and $k_t^b[P^\cdot]_0$, resp., at the moment of stopping of irradiation (at $t_{dark} = 0$) are of special interest in the polynominal models proposed.

By solving the differential equation systems: (5)—(7) and (5), (8), (9) one obtains the following expressions for the degree of double bond conversion as a function of time:

— Model 1

$$-\ln(1-p) = k_p[P^\cdot]_0 \int_0^t \exp\left[-\left(a_0 + \frac{1}{2}a_1 t + \frac{1}{3}a_2 t^2 + \frac{1}{4}a_3 t^3\right)t\right]dt \qquad (10)$$

— Model 2

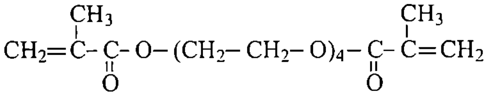
$$-\ln(1-p) = \int_0^t \frac{k_p[P^\cdot]_0}{\left(b_0 + \frac{1}{2}b_1 t + \frac{1}{3}b_2 t^2 + \ldots + \frac{1}{10}b_9 t^9\right)t + 1}dt \qquad (11)$$

where: p — *double bond conversion in the dark.*

Parameters of the models: $k_p[P^\cdot]_0$; $a_i = k_t^m$, i = 0—3 and $b_j[P^\cdot]_0 = k_t^b[P^\cdot]_0$, j = 0—9 were calculated using the nonlinear least square method.

EXPERIMENTAL

(Tetraethylene glycol) dimethacrylate [TETGDM, formula (I), Aldrich] was used as a model monomer.



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}O{-}(CH_2{-}CH_2{-}O)_4{-}\underset{O}{\underset{\|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 \qquad (I)$$

Experimental conditions were the same as described elsewhere [5]. Reaction rate profiles and conversions were determined at 40°C with differential scanning photocalorimetry. Polymerization was initiated with 366 nm light from a medium pressure Hg lamp (incident light intensity 1.3 mW/cm^2) in the presence of 2,2-dimethoxy-2-phenylacetophenone used at a concentration of 0.03 M. Irradiation was carried out in argon atmosphere.

The initiation in eight photoinduced polymerization processes was interrupted at various degrees of double bond conversion: 0.026, 0.052, 0.072, 0.106, 0.187, 0.287, 0.305 or 0.513. These conversions were denoted as the starting conversions.

RESULTS AND DISCUSSION

Figures 1—5 present results of calculations. Both models show that termination rate coefficients increase with time of dark the reaction t_{dark} (Figs. 1 and 2), which is a simple consequence of the rapid decrease in polymerization rate during the after-effect. In the absence of initiation, termination by radical trapping becomes increasingly important at deep polymerization stages [6], and our models properly reflect this situation (Model 2 describes the increasing termination rate coefficient during the dark reaction by a second order expression). This is consistent with our previous results [2, 3].

As can be seen in Fig. 3, the calculated values of $k_p[P^\cdot]_0$ products are practically the same for Model 1 and 2. Their dependence on starting conversion reflects their behavior during continuous illumination. Propagation rate coefficient k_p should be constant in the conversion range studied [1], so changes in $k_p[P^\cdot]_0$ value correspond to changes in active radical concentration during polymerization (maximum in $k_p[P^\bullet]_0$ value corresponds to the starting conversion where the maximum polymerization rate is observed).

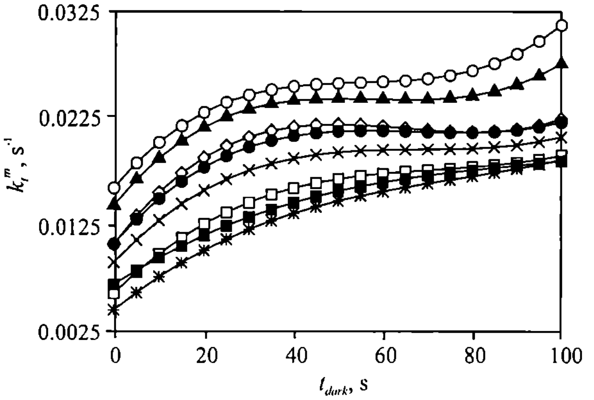


Fig. 1. Monomolecular termination rate coefficient k_t^m calculated from Model 1 as a function of time of the dark reaction for various starting conversions: O — 0.026; ▲ — 0.052; ◇ — 0.072, • — 0.106, x — 0.187, □ — 0.287, ✱ — 0.305, ■ — 0.513

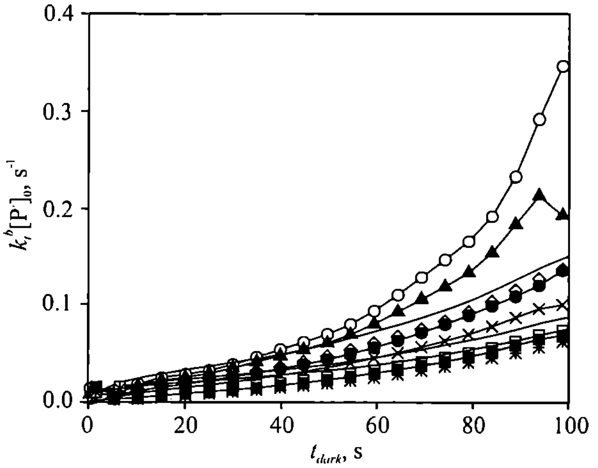


Fig. 2. Product of bimolecular termination rate coefficient k_t^b and macroradical concentration at the point of stopping irradiation $[P^\bullet]_0$ calculated from Model 2 as a function of tome of the dark reaction for various starting conversions. For symbols, see Fig. 1

Figure 4 shows the values of termination rate coefficients obtained as free terms of polynomials (7) and (9), *i.e.* after extrapolation to time of the dark reaction $t = 0$, as a function of starting conversion. Same, as in the case

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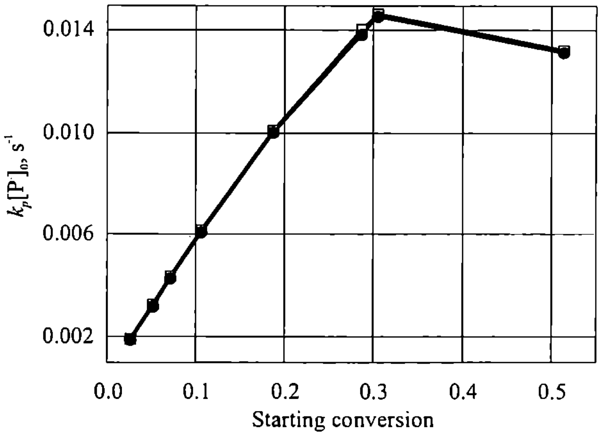

Fig. 3. Product of propagation rate coefficient k_p and macroradical concentration at the point of stopping irradiation $[P^\bullet]_0$ calculated from Model 1 (□) and Model 2 (•) as a function of starting conversion

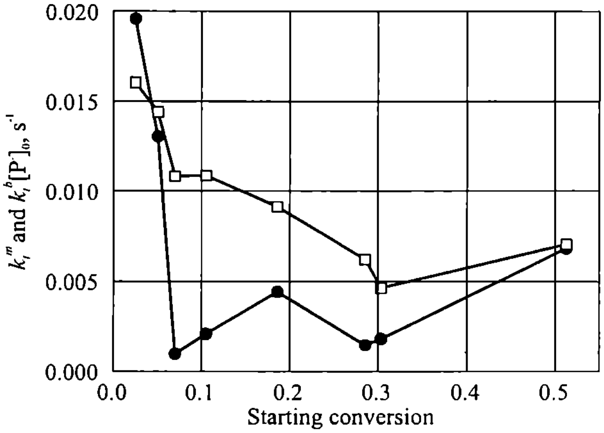

Fig. 4. Termination rate coefficients extrapolated to $t_{dark} = 0$: k_t^m calculated from Model 1 (□) and $k_t^b[P^\bullet]_0$ calculated from Model 2 (•) as a function of starting conversion.

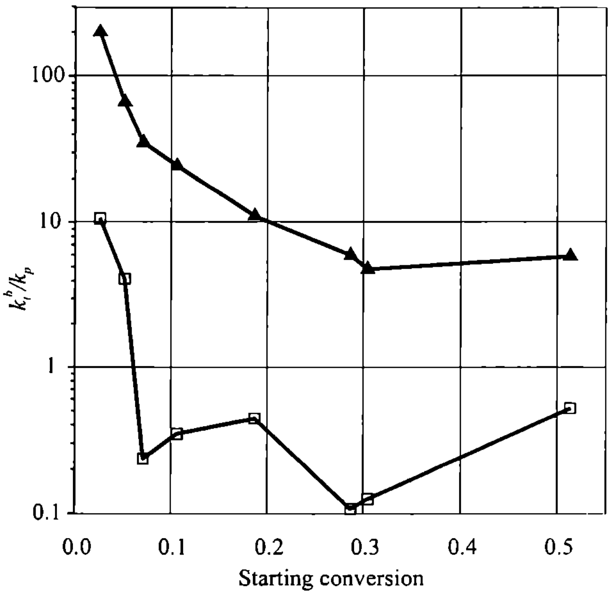

Fig. 5. The k_t^b/k_p ratio as a function of starting conversion; □ — from k_t^b $[P^\bullet]_0$ values obtained by extrapolation to $t_{dark} = 0$; ▲ — from $k_t^b[P^\bullet]_0$ values obtained after 100 s of the dark reaction

of $k_p[P^\cdot]_0$, they correspond to the values of termination rate coefficients during continuous illumination. The k_t^m, which is independent of radical concentration, initially decreases with starting conversion, suggesting that termination up to the maximum polymerization rate is dominated by the bimolecular mechanism, because Model 1, which is described by only one termination rate coefficient, has to represent all the termination processes taking place during the polymerization and k_t^b decreases with increasing conversion [1]. Monomolecular termination becomes increasingly important when the reaction rate begins to decrease (after its maximum) [2, 4] and k_t^m increases. Conversion dependence of $k_t^b[P^\cdot]_0$ is very similar to that of k_t^m, but one must remember that radical concentration changes during the reaction and the k_t^b/k_p ratio gives a better view on k_t^b behavior (Fig. 5). Conversion dependence of this ratio is typical for the bimolecular termination: a rapid decrease at the very beginning of the reaction and then a plateau [1]. Note that values of the k_t^b/k_p ratio highly depend on time of the dark reaction taken for calculations. However, similarity in $k_t^b[P^\cdot]_0$ and k_t^m values obtained for $t_{dark} = 0$ indicates that during the continuous initiation the parameters $k_t^b[P^\cdot]_0$ and k_t^m are not determined by the reaction order, and the difference in k_t^b and k_t^m results only from radical concentration.

Concluding we can say that termination rate coefficients can be expressed as a function of time during the after-effect. Conversion dependence of extrapolated to $t_{dark} = 0$ $k_t^b[P^\cdot]_0$ and k_t^m parameters appearing in two various termination models is similar.

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Rapid Communications

Przypominamy P.T. Autorom, że prowadzimy w naszym czasopiśmie dział typu **Rapid Communications**. Publikujemy w nim, **wyłącznie w języku angielskim, krótkie** (3—4 strony maszynopisu i ewentualnie 2—3 rysunki lub tabele) **prace oryginalne**, którym gwarantujemy szybką ścieżkę druku, co oznacza, że pojawią się one w czasopiśmie w okresie nieprzekraczającym 5 miesięcy od chwili ich otrzymania przez redakcję.