Eur. Polym. J. Vol. 25, No. 7/8, pp. 725–730, 1989
Printed in Great Britain.

0014-3057/89 $3.00 + 0.00

INITIATION OF POLYMERIZATION WITH SUBSTITUTED ETHANES—12. FREE RADICAL POLYMERIZATION OF METHYL METHACRYLATE AND STYRENE INITIATED WITH 3-METHOXYCARBONYL-3-METHYL-2,2,5,5-TETRAPHENYLHEXANEDINITRILE*

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(*Received* 31 *January* 1989)

Abstract—The title compound, the first member of a homologous series of oligomers formed by free radical polymerization of methyl methacrylate initiated by tetraphenylbutanedinitrile, was synthesized and its structure was determined by X-ray diffraction. The longest C—C bond of this molecule measures 1.628 Å and can be thermally split to give radicals. The activation energy of this dissociation was found to be 150 kJ/mol. The kinetics of the free radical polymerization of methyl methacrylate and styrene initiated with the title compound shows remarkable deviations from the ideal polymerization kinetics, indicating that primary radical termination might be the main chain termination reaction.

INTRODUCTION

In previous publications [1–11] the initiating characteristics of various tetraphenylethanes towards methyl methacrylate (MMA) and styrene were reported. It was found that tetraphenylbutanedinitrile (TPBD) initiates the free radical polymerization of MMA in a two step reaction.

TPBD dissociates thermally in two cyanodiphenylmethyl radicals which either add to a monomer molecule or combine with a growing radical. This primary radical termination is the main termination reaction in the first step, and oligomers which carry a cyanodiphenylmethyl group at each end of the chain are formed thereby. The polymerization rate, R_1, during this first step is [4]

$$R_1 = k_p k_s / k_a C_m^2, \qquad (1)$$

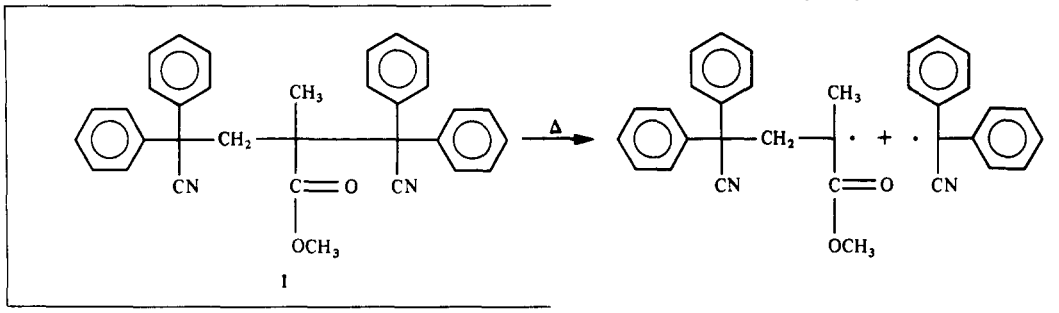
where k_p, k_s and k_a denote the rate constants of chain propagation, of the addition of a primary radical to a monomer molecule and of the primary radical termination, respectively. C_m is the monomer concentration.

In the second step, when almost all of the TPBD is consumed, these oligomers can reinitiate the polymerization by thermal cleavage of the C—C bond which is formed in the primary radical termination reaction, giving a cyanodiphenylmethyl radical and a "growing chain" radical. This homolytic dissociation is a consequence of the steric hindrance between the large substituents of the two quaternary carbon atoms. The polymerization rate, R_2, during this second step was found to be [4]

$$R_2 = k_2 \sqrt{C_i} C_m, \qquad (2)$$

where k_2 denotes the overall polymerization rate constant, and C_i is the initiator concentration.

This paper reports on the synthesis, structure and initiation properties of the first member of this homologous series of oligomers: 3-methoxycarbonyl-3-methyl-2,2,5,5-tetraphenylhexanedinitrile (**1**).



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EXPERIMENTAL PROCEDURES

Preparation of 3-methoxycarbonyl-3-methyl-2,2,5,5-tetraphenylhexanedinitrile (1)

A solution of 30 g TPBD and 25 ml MMA in 250 ml dry toluene was stirred at 80°C under argon for 3 days. The solvent was evaporated and the residue crystallized from methanol to yield 10 g of crude product containing 10% of TPBD which was removed by repeated recrystallization

*For part 11 see A. Bledzki, H. Balard and D. Braun. *Makromolek. Chem.* **189**, 2807 (1988).

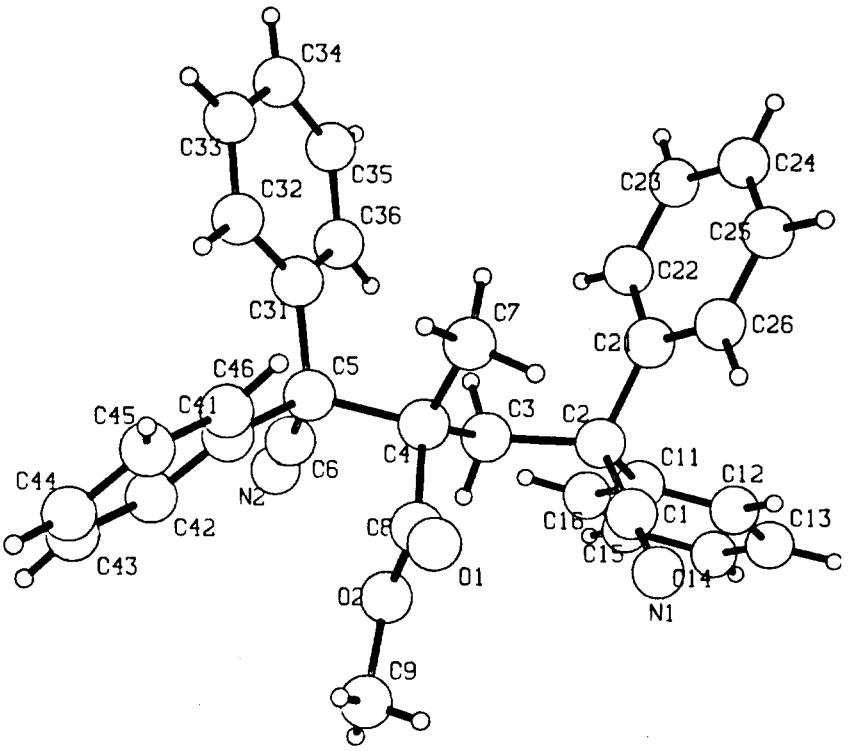

Fig. 1. Structure of **1** determined by X-ray diffraction.

from methanol, yielding 5.8 g pure product, m.p. 171°C. It decomposes on heating above the melting point, releasing MMA. Elemental analysis: $C_{33}H_{28}N_2O_2$ (484.6 g/mol), calc.: C 81.79%, H 5.82%, N 5.78%; found C 81.73%; H 5.79%; N 5.76%. ^{1}H NMR (Varian XL-100, $CDCl_3$, TMS, δ): 1.41 (s, 3H), 3.30 (s, 3H), 3.15 (d, 1H, J = 14 Hz), 3.83 (d, 1H, J = 14 Hz), 7.2–7.4 (m, 15H). MS (70 eV), m/z (%): 484 (6), 260 (7), 193 (35), 192 (100), 166 (21), 165 (37). i.r. (KBr, cm^{-1}): 2225 (CN), 1746 (C=O), 1230 (C—O).

Decomposition measurements of 1

Samples of 0.25 ml of a solution of **1** in tetrahydrofurane (0.02 mol/l) were sealed in glass ampoules and deposited in an oil bath for definite times at 100°, 110° and 127°C. The samples were then run through a low molecular weight gel permeation chromatography set, and the decomposition rate was calculated from the relation of the relative concentrations of decomposition products.

*X-ray structure determination of 1**

Colourless rods from ethylacetate; space group $P\bar{1}$, $a = 13.924(6)$ Å, $b = 12,234(6)$ Å, $c = 8.660(4)$ Å, $\alpha = 107.39(1)°$, $\beta = 99.59(1)°$, $\gamma = 106.66(1)°$, $V = 1296.31$ Å^3, $Z = 2$, $\rho_{calc} = 1.241$ g cm^{-3}, μ MoKα = 0.42 cm^{-1}, STOE–STADI-4 diffractometer, MoKα radiation, graphite monochromator, 4397 reflections ($\theta \leq 20°$) measured. 2238 reflections with $|F| \geq 2\sigma(F)$ corrected for background and geometrical factors were used for structure determination by direct methods (SHELX-86) and anisotropic refinement of all nonhydrogen atoms with geometrically positioned hydrogen atoms (SHELX-76), $R = 0.044$, $RW = 0.046$.

*The authors thank Dr H. Paulus (Institut für Physikalische Chemie, TH Darmstadt) for the measurement.

Monomers

MMA and styrene were purified by removing the stabilizer with dilute NaOH, drying with $CaCl_2$ and distillation over CaH_2 under nitrogen at reduced pressure.

Dilatometric measurements

Solutions of **1** in 15 ml of monomer (dry toluene was used as diluent for solution polymerizations), were degassed by three freeze–thaw cycles and transferred under argon into test tube-like dilatometers with volumes of about 12 ml; the capillaries had a dia of 0.8 mm. The polymerizations were carried out in an oil bath keeping the appropriate temperature (70°, 80° and 90°C) at ± 0.05°C. The monomer conversions were calculated from the relative volume contractions using literature data for the volume contraction constants of MMA [12] and styrene [13].

Molecular weight determination

The number-average molecular weights, M_n, were determined by gel permeation chromatography. The column set was calibrated with standard calibration samples of PMMA and polystyrene, respectively.

RESULTS AND DISCUSSION

X-ray structure determination

Figure 1 shows the structure of **1** determined by X-ray diffraction. The positional parameters and U_{eq} for nonhydrogen atoms are presented in Table 1 [14].

The bond length between the quaternary carbon atoms C5 and C4 (see Fig. 1) was found to be 1.628 Å, that is 0.09 Å larger than the normal bond length between two sp^3-carbon atoms. Even the C2—C3 bond (1.562 Å) is slightly longer than nor-

Table 1. Final atomic coordinates and thermal parameters of compound **1**

Atom	X/A	Y/B	Z/C	U(EQ)
N(1)	−0.0084 (02)	0.2951 (02)	0.2064 (03)	0.056 (01)
C(1)	0.0682 (02)	0.3024 (02)	0.2876 (03)	0.041 (01)
C(2)	0.1678 (02)	0.3078 (02)	0.3886 (03)	0.036 (01)
C(3)	0.2542 (02)	0.4345 (02)	0.4293 (04)	0.040 (01)
C(4)	0.2292 (02)	0.5530 (02)	0.4946 (03)	0.039 (01)
C(5)	0.3368 (02)	0.6722 (02)	0.5670 (03)	0.042 (01)
C(6)	0.4108 (02)	0.6432 (02)	0.4708 (03)	0.046 (01)
N(2)	0.4715 (02)	0.6216 (02)	0.4044 (03)	0.071 (01)
C(7)	0.1715 (02)	0.5509 (03)	0.6294 (04)	0.052 (01)
C(8)	0.1625 (02)	0.5673 (02)	0.3462 (03)	0.046 (01)
O(1)	0.0832 (01)	0.5869 (02)	0.3439 (03)	0.068 (01)
O(2)	0.2078 (01)	0.5585 (02)	0.2217 (02)	0.063 (01)
C(9)	0.1600 (04)	0.5813 (05)	0.0773 (06)	0.111 (03)
C(11)	0.1942 (02)	0.2018 (02)	0.2757 (03)	0.037 (01)
C(12)	0.1173 (02)	0.0856 (02)	0.2041 (03)	0.045 (01)
C(13)	0.1360 (03)	−0.0122 (03)	0.1030 (03)	0.053 (01)
C(14)	0.2310 (03)	0.0042 (03)	0.0726 (04)	0.061 (01)
C(15)	0.3085 (03)	0.1171 (03)	0.1443 (04)	0.065 (02)
C(16)	0.2899 (02)	0.2163 (02)	0.2457 (03)	0.049 (01)
C(21)	0.1525 (02)	0.2795 (02)	0.5462 (03)	0.037 (01)
C(22)	0.2379 (02)	0.2824 (02)	0.6590 (03)	0.048 (01)
C(23)	0.2251 (03)	0.2517 (03)	0.7974 (04)	0.061 (02)
C(24)	0.1286 (03)	0.2182 (03)	0.8245 (04)	0.079 (02)
C(25)	0.0445 (03)	0.2158 (03)	0.7149 (04)	0.079 (02)
C(26)	0.0562 (02)	0.2456 (02)	0.5760 (04)	0.057 (01)
C(31)	0.3925 (02)	0.6999 (02)	0.7527 (03)	0.047 (01)
C(32)	0.4021 (03)	0.8027 (03)	0.8820 (04)	0.081 (02)
C(33)	0.4525 (03)	0.8246 (05)	1.0465 (05)	0.107 (02)
C(34)	0.4937 (03)	0.7465 (05)	1.0849 (05)	0.091 (02)
C(35)*	0.4923 (03)	0.6464 (04)	0.9532 (06)	0.076 (02)
C(36)*	0.4439 (02)	0.6239 (03)	0.7880 (05)	0.055 (02)
C(41)	0.3186 (02)	0.7858 (02)	0.5436 (03)	0.041 (01)
C(42)	0.3731 (03)	0.8471 (03)	0.4591 (04)	0.093 (02)
C(43)	0.3584 (04)	0.9495 (04)	0.4400 (05)	0.127 (03)
C(44)	0.2878 (03)	0.9918 (03)	0.5024 (04)	0.083 (02)
C(45)	0.2327 (02)	0.9337 (03)	0.5884 (05)	0.065 (02)
C(46)	0.2481 (02)	0.8316 (03)	0.6083 (04)	0.061 (01)
C(35A)*	0.4333 (15)	0.6463 (18)	1.0054 (26)	0.015 (92)
C(36A)*	0.3854 (14)	0.6167 (17)	0.8390 (25)	0.012 (92)

*A disorder, observed in the region of the benzene ring C(31)–C(36) was corrected by splitting the positions of C(35) and C(36) into positions C(35), C(36) (s.o.f. 0.9) and C(35A), C(36A) (s.o.f. 0.1).

mal. The C2—C3—C4 bond angle measures 118.99° instead of about 110° for a sp^3-carbon atom. These structural data prove the steric strain of this molecule according to the theory of Rüchardt and Beckhaus [15], that the first effect of steric hindrance is the stretching of bond angles, and if this does not minimize the tensions, secondly the bond lengths should increase.

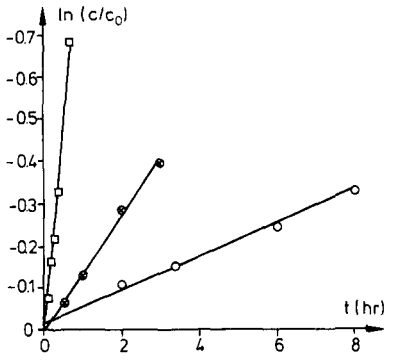

Fig. 2. Dependence of $\ln(C/C_0)$ vs time for the decomposition of **1** in tetrahydrofurane: ○, 100°C; ⊗, 110°C; □, 127°C.

Decomposition of 1

The decomposition of **1** was followed by gel permeation chromatography of solutions of **1** in tetrahydrofuran which had been thermostated for definite times at 100°, 110° and 127°C, respectively. It was found that **1** decomposes to TPBD and MMA and small amounts of diphenylacetonitrile, which is probably the product of a side reaction of the cyanodiphenylmethyl radical with the solvent. The decomposition products were also identified by ^{1}H NMR spectroscopy.

Figure 2 shows the changes in the concentration of **1** with time during thermostating. From these data the decomposition rate constants, k_d, were calculated and plotted in an Arrhenius diagram which is shown in Fig. 3.

Regression analysis of the straight line of Fig. 3 yields

$$\ln k_d = 36.8 - \frac{18000}{T}. \qquad (3)$$

Thus, the activation energy of the decomposition reaction is 150 kJ/mol.

Polymerization kinetics

1 was used as initiator for the free radical polymerization of MMA and styrene. Figure 4 shows the

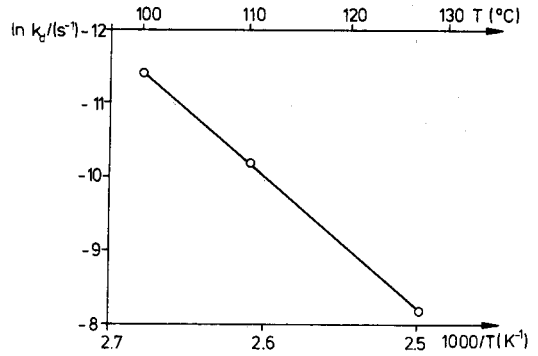

Fig. 3. Arrhenius plot for the rate constants of the decomposition of **1**.

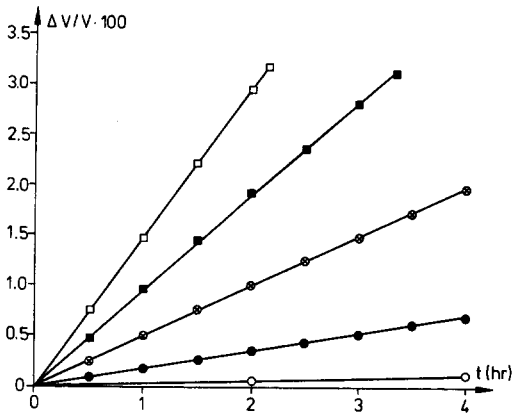

Fig. 5. Relative volume contraction vs time for the polymerization of MMA in toluene with various monomer concentrations at 90°C. ○, 1.735 mol/l; ●, 3.48 mol/l; ⊗, 5.19 mol/l; ■, 6.91 mol/l; □, 8.62 mol/l; C_i = 3.8 mmol/l.

relative volume contraction during the bulk polymerization of MMA at 90°C initiated with various amounts of **1** and Fig. 5 shows the relative volume contraction during the solution polymerization of MMA at 90°C in toluene with various monomer concentrations.

In both cases a linear dependence between the volume contraction and reaction time is observed. For the polymerization of styrene the volume contraction vs time curves look similar and are therefore not depicited here.

Figures 6 and 7 show the dependencies of the reaction rate from the initiator concentration and the monomer concentration, respectively.

The relations between the number-average molecular weights and the initiator and monomer concentration, respectively, for the polymerization of MMA with **1** are represented in Figs 8 and 9.

It can be seen from these plots that there is no linear relationship between the reaction rate and the initiator and monomer concentration, respectively. The power of the initiator concentration ranges from 0.34 (MMA, low concentration at 70°C) to 0.21 (MMA, high concentration at 90°C). For the monomer concentration the power is about 2, decreasing with increasing monomer concentration to

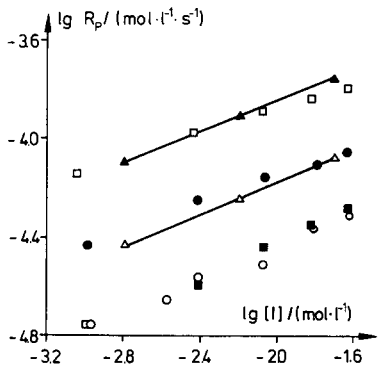

Fig. 6. Dependence of the reaction rate on the concentration of **1** for the bulk polymerization of: ■, styrene at 80°C; ○, MMA at 70°C; ●, MMA at 80°C; □, MMA at 90°C, and calculated from equation (9) for MMA at △, 80°C and ▲, 90°C.

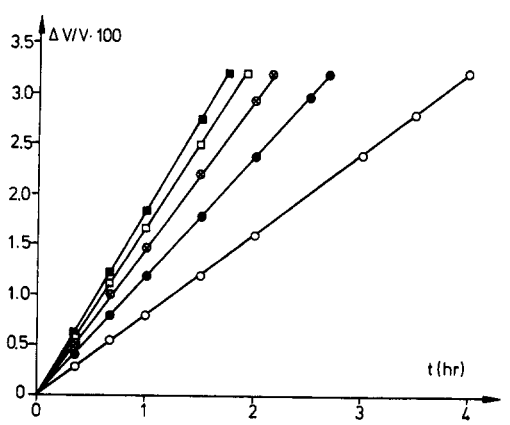

Fig. 4. Relative volume contraction vs time for the bulk polymerization of MMA with various amounts of **1** at 90°C. ○, 0.89 mmol/l; ●, 3.61 mmol/l; ⊗, 8.26 mmol/l; □, 14.63 mmol/l; ■, 23.06 mmol/l.

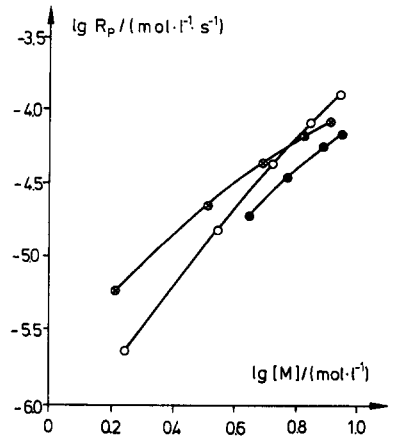

Fig. 7. Dependence of the reaction rate on the monomer concentration for the polymerization of: ⊗, styrene at 90°C; C_i = 9.47 mmol/l; ●, MMA at 80°C; C_i = 8.43 mmol/l; ○, MMA at 90°C; C_i = 8.3 mmol/l, with **1** in toluene.

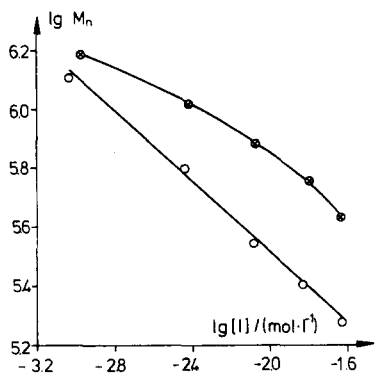

Fig. 8. Dependence of the number-average molecular weight on the concentration of **1** for the bulk polymerization of: ⊗, MMA at 80°C; ○, MMA at 90°C.

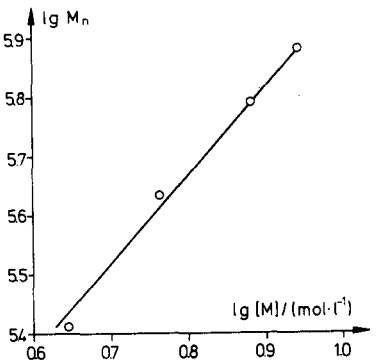

Fig. 9. Dependence of the number-average molecular weight on the monomer concentration for the polymerization of MMA at 80°C with **1**, $C_i = 8.43$ mmol/l.

almost 1 in the case of styrene. These data indicate a nonideal reaction mechanism, which may look as follows:

$$I \xrightarrow{k_d} Q + R \qquad v_d = k_d C_i \tag{4}$$

$$Q + M \xrightarrow{k_s} R \qquad v_s = k_s C_q C_m \tag{5}$$

$$R + M \xrightarrow{k_p} R \qquad v_p = k_p C_r C_m \tag{6}$$

$$R + Q \xrightarrow{k_a} P' \qquad v_a = k_a C_r C_q \tag{7}$$

$$2R \xrightarrow{k_t} P \qquad v_t = k_t C_r^2 \tag{8}$$

where I denotes compound **1**, Q the cyanodiphenylmethyl radical, R the growing chain radical (the radical formed by dissociation of I is assumed to be identical with R), M the monomer, P′ the polymer formed by primary radical termination and P the polymer formed by combination or disproportionation termination; C_i, C_q, C_r and C_m are the corresponding concentrations.

Considering the following assumptions:

—the addition of a monomer molecule to the "growing chain" radical formed in reaction (4) is faster than its decomposition to a monomer molecule and a cyanodiphenylmethyl radical;
—the dissociation of P′ (which carries the same fissionable C—C bond as I owing to primary radical termination) to Q and R is negligible at low conversions;
—no combination reaction of two molecules of Q to give TPBD;
—steady state conditions for Q and R, i.e. $v_d = v_s + v_a$ and $v_d + v_s = v_a + v_t$; and
—$v_a \gg v_s$,

it can be calculated that

$$C_q = \frac{k_d C_i}{k_a C_r}$$

and hence

$$C_r = \left(\frac{k_d k_s}{k_t k_a} C_i C_m\right)^{1/3}.$$

Neglecting the monomer consumption in reaction (5), which is permissible at high polymerization degrees, it follows that the overall polymerization rate, R_p, is

$$R_p \equiv v_p = k_p \left(\frac{k_d k_s}{k_t k_a}\right)^{1/3} C_i^{1/3} C_m^{4/3}. \tag{9}$$

Titzschkau [16] found for the dependence of the k_s/k_a ratio from temperature for the polymerization of MMA initiated by TPBD

$$\ln(k_s/k_a) = -4.66 - \frac{5953}{T}. \tag{10}$$

Taking k_s/k_a values from this equation, and using literature data [17] for the estimation of k_p and k_t together with k_d values from equation (3), values of R_p for the polymerization of MMA with I at 80°C and 90°C were calculated by equation (9) and plotted in Fig. 6. As can be seen, the calculated lines coincide quite well with the experimental data, so it may be concluded, that the above outlined reaction scheme is valid within the limits given by the assumptions made on its elaboration.

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