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Pulsed laser terpolymerization of styrene, methyl methacrylate and methyl acrylate

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SUMMARY:
   The propagation rate coefficient of the terpolymerization of styrene, methyl methacrylate and methyl acrylate in bulk was successfully determined at three different monomer compositions. The temperature was varied between 18 and 80 °C. The resulting data at 50 °C were not in agreement with predictions according to the terminal model with binary reactivity ratios that have been determined by fitting copolymer composition data with the terminal model. This indicates that here also the penultimate unit affects the kinetics.

Introduction

   Pulsed laser polymerization (PLP) experiments were conducted to determine the average propagation rate coefficient $(\bar{k}_p)$ of the bulk terpolymerization of styrene (S), methyl methacrylate (MMA) and methyl acrylate (MA) at three different monomer compositions. These data were needed for a kinetic analysis of emulsion terpolymerizations of S, MMA and MA [1].

   The average propagation rate coefficient of a particular free radical polymerization system can be determined from the differential log molecular weight distribution of the polymer prepared with PLP under certain conditions. The inflection point at the low molecular weight side of the PLP peak in the differential log molecular weight distribution is a direct measure of the propagation rate of a polymeric radical [2]. The monomer concentration being known, a value for the propagation rate constant/coefficient can be calculated. The theoretical considerations behind this technique for determining propagation rate constants/coefficients have been discussed extensively in the literature [2].

Experimental part

   The polymerization experiments were carried out with a Lambda Physik LPX110iMC excimer laser (wavelength 351 nm). The repetition rate was varied between 1 and 20 Hz and the total pulse time between 2 and 20 min, depending on the polymerization temperature, which was varied between 18 and 80 °C. As photo-initiator Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone, Ciba-Geigy) at a concentration of 5 mmol/dm^3 was used. Gel-permeation chromatography (GPC) was done on a chromatographic system equipped with two Shodex linear columns (GPC KF80M, 30 cm) and a refractive index detector (Waters Model 410). Tetrahydrofuran (THF) was used as the eluent, flow rate was 1 cm^3/min. Monomer concentrations C_M were calculated by linear interpolation and extrapolation of density data of the pure monomers at 25 and 50 °C, by assuming ideal mixing.

Results and discussion

The differential log molecular weight distributions $(\mathrm{d}W(\log(M))/\mathrm{d}\log(M))$ needed for the determination of $\bar{k}_p$ were obtained by multiplying the GPC trace $(\mathrm{d}W(\log(M))/\mathrm{d}V_{el})$ with $\mathrm{d}V_{el}/\mathrm{d}\log M$ (the reciprocal of the derivative of the calibration curve, V_{el} is the elution volume), see Eq. (1)[3].

$$\frac{\mathrm{d}W(\log(M))}{\mathrm{d}\log(M)} = \frac{\mathrm{d}W(\log(M))}{\mathrm{d}V_{el}} \frac{\mathrm{d}V_{el}}{\mathrm{d}\log(M)} \tag{1}$$

Universal calibration was applied to correct for the difference in hydrodynamic volume of the polystyrene standards used in GPC and that of the S-MMA-MA terpolymers. The molecular weight of a terpolymer $(M_{terpolymer})$ with a fraction of monomer i in the terpolymer equal to F_i, was calculated according to Eq. (2).

$$M_{terpolymer} = M_0^{terpolymer} \sum_{i=1}^{3} \left(\frac{F_i \cdot M_i}{M_0^i} \right) \tag{2}$$

where 1, 2, 3 represent the pertaining monomers, M_0^i is the molar mass of monomer i, and $M_0^{terpolymer}$ the average molar mass of the monomers in the terpolymer at a specific terpolymer composition. M_S is the molecular weight obtained after calibration with monodisperse polystyrene standards, and M_{MA} and M_{MMA} are the molecular weights calculated from M_S with universal calibration using the Mark-Houwink coefficients of poly(MA) and poly(MMA), respectively. The Mark-Houwink coefficients used are given in Tab. 1.

Tab. 1. Mark-Houwink coefficients used for universal calibration of the terpolymers of styrene (S), methyl methacrylate (MMA) and methyl acrylate (MA)

Coefficients	S[4]	MMA[5]	MA[4]
$K/(\mathrm{dm}^3/\mathrm{kg})$	$1{,}62 \cdot 10^{-2}$	$1{,}78 \cdot 10^{-2}$	$0{,}788 \cdot 10^{-2}$
a	0,71	0,69	0,885

The differential molecular weight distribution obtained in this way is used to determine the inflection point connected with $\bar{k}_p$. This procedure to calculate the molecular weight of the ter(co)polymer in the inflection point is different from the procedure applied by Davis et al.[4]. For the determination of the kinetic chain length of the copolymers of S and MA, and of S and butyl acrylate they first determined the inflection point without universal calibration (i.e., as if the polymer were pure polystyrene), and then also after calibration with the Mark-Houwink coefficients for polystyrene and poly(methyl acrylate)/poly(butyl acrylate), as if the polymer were pure poly(methyl acrylate)/poly(butyl acrylate). The two chain lengths thus obtained were averaged according to the molar composition of the copolymer. The resulting average chain length was defined as being the chain length of the copolymer. In the present case the whole distribution is recalculated by an averaging procedure according to Eq. (2), and then the inflection point is determined. Both methods give estimations for the true
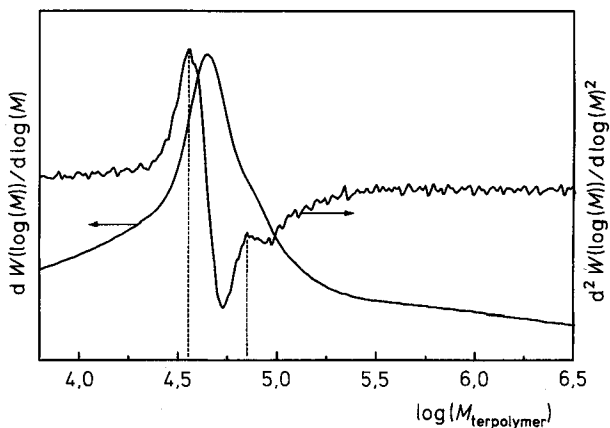
Fig. 1.   (left y-axis) Differential log molecular weight distribution of a S-MMA-MA terpolymer prepared with PLP at 50 °C. f_S, f_{MMA}, f_{MA} = 0,186, 0,248, 0,565, repetition rate $1/\Delta t$ = 10 Hz, total pulse time is 4 min, concentration of initiator is 5 mmol/dm^3. The derivative is also given (right y-axis)

value of the molecular weight at the inflection point. For a terpolymer with F_S = F_{MMA} = F_{MA} = 0,33 the difference in $\bar{k}_p$ values determined according to both methods is less than 1%.

It is expected from literature data on $\bar{k}_p$ for the copolymerizations of S and MA [1, 4] and of S and MMA [6–8] that $\bar{k}_p$ of this terpolymer, at the compositions investigated, will not be much higher than that of S. Therefore, the same experimental conditions were chosen as found optimal for PLP of S. By varying the temperature over a wide range, the possibility of artefacts going unnoticed can be minimized. The artefacts may, for instance, be due to relatively fast transfer reactions like in the pure acrylate systems [9]. The three monomer compositions investigated are: $(f_S, f_{MMA}, f_{MA} =)$ (A) 0,166, 0,229, 0,606, (B) 0,186, 0,248, 0,565, (C) 0,333, 0,333, 0,333 (f_i is the molar fraction of i in the monomer feed mixture).

In Fig. 1 is depicted the log molecular weight distribution of a S-MMA-MA terpolymer, prepared with PLP at 50 °C with a monomer feed composition (B). As can be seen, the PLP peak is quite apparent, and so is the inflection point at the low molecular weight side, indicated by the maximum in the derivative (right y-axis). The occurrence of a second inflection point (overtone) at a molecular weight almost exactly twice that of the first inflection point is a strong indication that the first inflection point is a good measure of the propagation rate: the molecular weight at the inflection point $(M_{terpolymer})$ is a good measure of the kinetic chain length a polymeric radical attains by propagating during the time passing between two pulses multiplied by the average molecular weight of the monomer units in the terpolymer $(M_0^{terpolymer})$. That kinetic chain length is equal to the ratio of the time between two pulses (Δt) and the time scale for one propagation step $(\bar{k}_p \cdot C_M)^{-1}$, where C_M is the monomer concentration in the experiment, so the following equation holds:
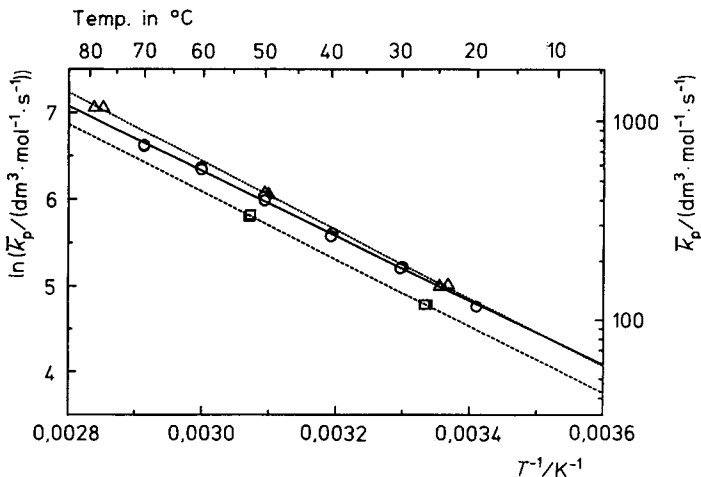
Fig. 2. The natural logarithm of the average propagation rate coefficient (left y-axis), $\ln(\bar{k}_p)$, and $\bar{k}_p$ on a logarithmic scale (right y-axis), vs. inverse temperature (bottom x-axis, $1/T$), and vs. temperature (top x-axis). Termonomer compositions f_S, f_{MMA}, f_{MA}: (A) 0,166, 0,229, 0,606 ($\cdots$, $\triangle$), (B) 0,186, 0,248, 0,565 (———, $\circ$), (C) 0,333, 0,333, 0,333 (— — —, $\square$). The lines are fits with the Arrhenius equation (see Tab. 2)

$$M_{\text{terpolymer}} = \frac{\text{time between pulses}}{\text{time scale for propagation}} \cdot M_0^{\text{terpolymer}} = \bar{k}_p \cdot C_M \cdot \Delta t \cdot M_0^{\text{terpolymer}} \quad (3)$$

In Fig. 2 the $\bar{k}_p$ values thus obtained for three monomer compositions are presented in an Arrhenius plot. For each composition the data were fitted with the Arrhenius expression. For data sets A and B this resulted in good fits, which is an indication that the data are no artefacts (data set C comprises only two different temperatures). Because the values found for these compositions are close together, it can be assumed that $\bar{k}_p$ does not show a strong dependence on the monomer composition, like the systems S-MA and S-MMA at low to intermediate fractions of S.

In Tab. 2 the Arrhenius parameters and the values for $\bar{k}_p$ at 50 °C for each composition are presented. A relative error of 15% is assumed, 10% stemming from deviations in the Mark-Houwink parameters, and additional 5% from GPC errors. Note that $\bar{k}_p$ is an average propagation rate *coefficient* composed of rate *constants*, ratios of rate constants, etc. The Arrhenius parameters do, therefore, not pertain to a single rate constant. It can be seen that $\bar{k}_p$ increases slowly with increasing f_{MA}, which was expected.

For both the copolymerization system S-MMA[6-8] at 25 and 40 °C, and for the copolymerization system S-MA[1,4] at 25 and 50 °C it was clearly shown that $\bar{k}_p$ as a function of composition cannot be fitted with the terminal model when using the reactivity ratios obtained by fitting the composition data with the terminal model. By

Tab. 2. Arrhenius parameters (pre-exponential factor A and activation energy E_{act}) and values of the average terpolymer propagation rate coefficient measured at 50 °C ($\bar{k}_p$), and calculated with the terminal model ($\bar{k}_p^{term}$)

f_S, f_{MMA}, f_{MA}	$A/(dm^3 \cdot mol^{-1} \cdot s^{-1})$	$E_{act}/(kJ \cdot mol^{-1})$	$\bar{k}_p/(dm^3 \cdot mol^{-1} \cdot s^{-1})$	$\bar{k}_p^{term}/(dm^3 \cdot mol^{-1} \cdot s^{-1})$
0,166, 0,229, 0,606	$10^{7,96}$	32,9	433 ± 65	710 ± 55
0,186, 0,248, 0,565	$10^{7,62}$	31,1	393 ± 60	696 ± 48
0,333, 0,333, 0,333	$10^{7,72}$	32,4	305 ± 45	627 ± 23

Tab. 3. Reactivity ratios (r_{ij}) and homopropagation rate constants (k_p) used for calculating $\bar{k}_p^{term}$ in Tab. 2

i, j	r_{ij}	$k_p/(dm^3 \cdot mol^{-1} \cdot s^{-1})$
S, MMA	r_{SMMA} = 0,48 ± 0,03 [10]	258 [12]
S, MA	r_{SMA} = 0,73 ± 0,05 [11]	
MMA, S	r_{MMAS} = 0,42 ± 0,09 [10]	616 [14]
MMA, MA	r_{MMAMA} = 2,09 ± 0,3 [13]	
MA, S	r_{MAS} = 0,19 ± 0,05 [11]	8900 [9]
MA, MMA	r_{MAMMA} = 0,22 ± 0,05 [13]	

invoking a penultimate model the $\bar{k}_p$ data could be fitted very well. That this is the case also for this terpolymerization system, is shown by the following. We calculated values for $\bar{k}_p$ with the terminal model ($\bar{k}_p^{term}$) by using the reactivity ratios (obtained from fitting copolymer composition data with the terminal model) and the homopolymerization k_p values given in Tab. 3. It can be seen in Tab. 2 that these calculated values are not in agreement with the experimental values: much higher values are obtained for each composition, as was also the case in the copolymer systems S-MA and S-MMA. The errors indicated in $\bar{k}_p^{term}$ are calculated by assuming a worst case for the errors in the reactivity ratios in Tab. 3. It is very likely that, as in the case of the above mentioned copolymer systems, the penultimate model will have to be used here as well. Although it should be possible to use the values of the reactivity ratios k_{jii}/k_{iii} ($=s_i$) as determined by various authors [1,4,6-8] for S-MMA and S-MA, the number of extra unknown parameters (eight) still exceeds the number of experimental data points, so no parameter values can be derived from the data.

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