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Measurement of chain transfer to monomer constants in ketene acetal homo- and copolymerization

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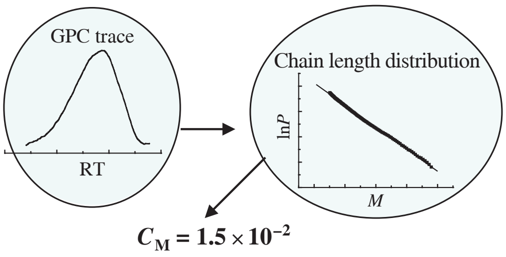
The chain transfer to monomer constants (C_M) in homopolymerization of 2-methylene-1,3-dioxepane and its copolymerization with styrene are determined under different conditions using the chain length distribution analytical method. The obtained chain transfer constant value $C_M = (1.2–1.6) \times 10^{-2}$ is 2–3 orders of magnitude higher than that for polymerization of vinyl monomers such as styrene, MMA and others. Therefore, the chain transfer to monomer is the main chain-growth termination reaction in radical ring-opening polymerization of ketene acetals.



Keywords: chain transfer to monomer, ketene acetals, ring-opening, radical polymerization, chain length distribution.

Radical ring-opening polymerization (rROP) of cyclic ketene acetals (CKAs) is one of the promising approaches to the synthesis of (bio)degradable polymers. The method successfully combines the simplicity, reliability and versatility of radical polymerization with the capability to generate the aliphatic polyester chain hydrolysable under mild basic or enzymatic conditions.[1,2] Radical copolymerization of CKAs with vinyl monomers leads to the incorporation of ester units into the polymeric hydrocarbon backbone and formation of (bio) degradable poly(vinyl-co-esters). In this case, the vinyl polymers in question only slightly change their composition and retain the original set of properties.

However, there are very few reports on the mechanism and kinetics of the rROP reaction of CKAs. It is known that the kinetic features of the radical polymerization of these compounds differ in many respects from those for the polymerization of vinyl monomers. In particular, the polymerization is characterized by an increased reaction rate order with respect to the monomer, and auto-deceleration of polymerization is observed instead of auto-acceleration at medium and high conversions.[3] Another distinctive feature of the rROP reaction of CKAs is the low molecular weight M of the resulting polymers. For polymers from ketene acetals, M_n is typically ~10^3–10^4.[4]

In addition, the molecular weight of the resulting polymer is weakly dependent on the experimental conditions (temperature, concentration and nature of the initiator). These statements can be confirmed using the example of radical polymerization of 2-methylene-1,3-dioxepane (MDO) (Table S1, Online Supplementary Materials). Systematic studies have shown that M_n of poly(MDO) is practically independent of either temperature[4] or concentration of the initiator[5] and randomly falls in the range from 6000 to 13000. The reason for this phenomenon was not discussed earlier.

In the present work, using the example of MDO polymerization, we have determined for the first time the chain transfer to monomer constants (C_M) *in situ* in MDO homopolymerization and its copolymerization with styrene.

To estimate the value of the chain transfer to monomer constants, we used the method of chain length distribution (P) linearization.[6] It is known that if the chain transfer to monomer dominates as the termination mechanism, then a ln$P$ *vs.* M plot is well linearized in the high molecular weight region.[7] In this case, the value of the chain transfer to monomer constants (C_M) is then determined as the straight-line slope of the plot according to the simple equation

$$\frac{d\ln P}{dM} = -C_M/m, \qquad (1)$$

where M is the molecular weight of the macromolecule, m is the molecular weight of the monomer unit.

The chain length distribution of macromolecules, $P(M)$, can be easily obtained from the original gel permeation chromatography (GPC) trace G(RT), where RT is retention time, as follows:[8]

$$\ln P(M) = \text{const} + \ln\frac{G(\text{RT})}{M^2}. \qquad (2)$$

Figure 1 shows the high molecular weight wings of the ln$P$ *vs.* M plots for poly(MDO) samples obtained at various concentrations of the di-*tert*-butyl peroxide (DTBP) radical initiator at 125 °C. In all cases, the linear region of the plot can be observed, which becomes more extensive as the initiator concentration increases. This confirms our assumptions about the high probability of the chain transfer to monomer.

The calculated C_M values are 1.60×10^{-2}, 1.25×10^{-2} and 1.25×10^{-2} at the initiator concentration of 0.18, 0.05 and 0.015 mol dm^{-3}, respectively, or on average, $C_M = (1.4 \pm 0.1) \times 10^{-2}$.

Similar results were obtained for poly(MDO) samples prepared using an AIBN radical initiator at 70 °C (Figure 2). The C_M values were 0.99×10^{-2}, 1.3×10^{-2} and 1.4×10^{-2} at an AIBN concentration of 0.17, 0.01 and 0.001 mol dm^{-3}, respectively.

The chain length distribution linearization method also allows one to find the value of the chain transfer constant from the styrene radical to MDO. It is known[9] that upon radical copolymerization of

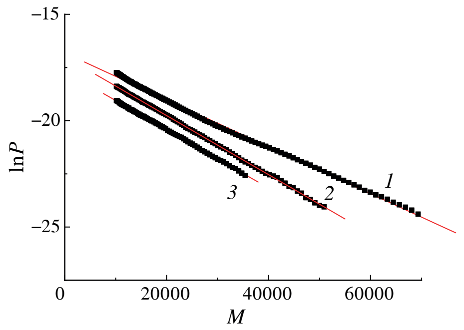


Figure 1 Linearized chain length distribution for poly(MDO) macromolecules in the coordinates of equation (1); [DTBP] = (*1*) 0.18, (*2*) 0.05 and (*3*) 0.015 mol dm^{-3}, 125 °C (experimental details of the synthesis are given in Online Supplementary Materials).

styrene with MDO in the presence of excess of styrene, MDO practically does not enter into copolymerization and serves only as a solvent for styrene. According to NMR analysis data, at the 0.25 molar fraction of MDO in the initial feed, the copolymerization product is almost pure polystyrene. It turned out that for this system the high molecular weight end of the ln*P* plot is also well linearized in the coordinates of equation (1) (Figure 3). The value of the chain transfer constant from the styrene growth radical to MDO, calculated by formula (3), also turned out to be quite high, $C_M = 1.5 \times 10^{-2}$:

$$\frac{d\ln P}{\mathrm{d}M} = -C_\mathrm{M}\frac{[\text{styrene}]}{[\text{MDO}]}/m. \tag{3}$$

Comparing the C_M values for MDO with those published for vinyl monomers (for example, $C_M = 5 \times 10^{-5}$ for styrene and $C_M = 1 \times 10^{-5}$ for MMA),[10] we can conclude that the chain transfer to MDO occurs with a probability 3 orders of magnitude higher than that for vinyl monomers. From these data, it can be clearly concluded that the chain transfer to monomer is the dominant termination mode in the radical polymerization of MDO. It is known that in such processes the molecular weight and molecular weight distribution of polymer do not depend on the initiator concentration, since the rates of both the chain growth and the chain termination are directly proportional to the monomer concentration (Table 1).

For example, there is the case of polymerization of allylic monomers by the mechanism of degradative chain transfer,[11] where $C_M \approx 10^{-1}$. It is this circumstance that can explain the low molecular weight of ketene acetal polymers, being practically independent of the initiator concentration.

Table 1 Molecular weight characteristics of poly(MDO) obtained under various initiator DTBP concentrations at 125 °C.[a]

[DTBP]/mol dm^{-3}	Conversion (%)	M_n/kDa	M_w/M_n
0.015	8.2	7.7	1.9
0.05	10	10.5	1.5
0.18	17.5	9.2	1.9

[a] M_n – number average molecular weight, M_w – weight average molecular weight.

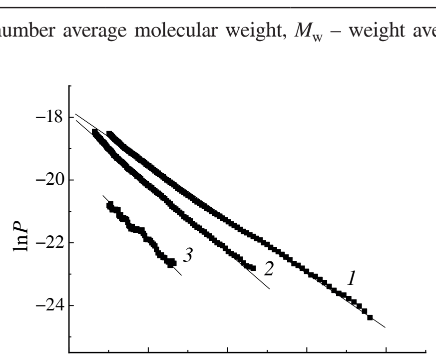


Figure 2 Linearized chain length distribution for poly(MDO) macromolecules in the coordinates of equation (1); [AIBN] = (*1*) 0.17, (*2*) 0.01 and (*3*) 0.001 mol dm^{-3}, 70 °C.

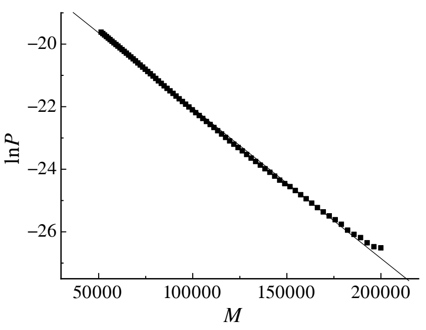


Figure 3 Linearized chain length distribution for polysterene macromolecules in the coordinates of equation (3) for the polymerization of styrene in the presence of 25 mol% MDO; [AIBN] = 0.17 mol dm^{-3}, 70 °C.

The established fact of the high value of C_M also has practical significance. A lot of reports on the feasibility of living controlled radical polymerization under SFRP, ATRP and RAFT conditions have been published earlier.[1,2] When carrying out the controlled synthesis of ketene acetal polymers, the high value of C_M and the restrictions it imposes on the limiting value of M_w should be taken into account.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7678.

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