Polymer Bulletin 9, 515-517 (1983)

Polymer Bulletin

Minimization of Molecular Heterogeneity in Radical Polymerization Application for Central Block Syntheses in Threeblock Copolymers

Th. Mezger and H.-J. Cantow

Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus,
Stefan-Meier-Straße 31, D-7800 Freiburg i. Br., Federal Republic of Germany

SUMMARY

The molecular heterogeneity in free radical polymerization can be minimized up to high initiator conversions, when initiator concentration or decomposition rate are adjusted properly. Experimental results on styrene polymerization in benzene, with AIBN as initiator, confirm the validity of the calculations.

Minimization of molecular heterogeneity is useful particularly for block copolymer syntheses involving radical polymerization steps initiated by macroinitiators.

INTRODUCTION

Free radical polymerizations are known to yield high polydispersities of the final polymer, when performed up to high conversions, mainly due to the variation of reactant concentrations within wide limits during the course of the reaction and, consequently, due to the superposition of the SCHULZ-FLORY distributions created at every instant of the polymerization. This fact may be considered disadvantageous in block copolymer syntheses via macroinitiator particularly, where polydispersity of the blocks means chemical heterogeneity of the product. Essentially quantitative conversion of the macroinitiator is desired, however.

The study on this problem had been stimulated by our interest to prepare block copolymers containing cellulose derivatives (1-5). Radical polymerization turned out to be the most promising method, since it is less sensitive to impurities when compared with anionic polyreactions or with endgroup coupling. The synthesis of a symmetrical cellulose triester macroinitiator of the type CD-I-CD - CD = cellulose deivative - tributyryl or tri(propionyl-acetyl) cellulose - and -I-I- = initiator - -CONH-ar-S-S-ar-NHCO- - is described elsewhere, as well as the block copolymer preparation and the polymer properties. Styrene and chloroprene have been used as the monomers (1, 3, 4).

In the following, the evaluation of the kinetic scheme of radical polymerization will be given with respect to initiator conversion. It will be shown that the polydispersity of the product has not necessarily to be high even at high initiator conversion, if initial initiator concentration or decomposition rate are adjusted properly.

RESULTS AND DISCUSSION

Assuming termination by combination exclusively and applying the usual simplifying assumptions, neglecting volume changes as well as viscosity effects and assuming first order decrease in initiator concentration, the kinetic scheme of free radical polymerization gives for the instantaneous number average degree of polymerization

$$\overline{P}_{n,o} = k_p[M]_o/(k_t k_d f[I]_o)^{1/2} \qquad (1)$$

$$\overline{P}_{n,t} = k_p[M]_t/(k_t k_d f[I]_o \exp(-k_d t))^{1/2} \qquad (2)$$

(Volume changes may be accounted for by the procedures proposed By TOBOLSKI et al. (6) or by NISHIMURA (7) . The absence of viscosity effects has to be ascertained by proper experimental conditions, e. g. by polymerizing in solution, for obvious reasons.)

Together with expression (3), which was given first by TOBOLSKI (8) (dead end treatment), one easily obtains the function of $\ln(\overline{P}_{n,t}/\overline{P}_{n,o})$ varying with t (eq. (4)):

$$\ln([M]_t/[M]_o) = 2\,k_p(f[I]_o/k_t k_d)^{1/2}\,(\exp(-k_d t/2) - 1) \qquad (3)$$

$$\ln(\overline{P}_{n,t}/\overline{P}_{n,o}) = (k_d t/2) + \ln([M]_t/[M]_o) \qquad (4)$$

Substituting K for $k_p(f/k_t k_d)^{1/2}$ and x_I for $1 - [I]_t/[I]_o = 1 - \exp(-k_d t)$, eq. (4) comes into the form

$$\ln(\overline{P}_{n,x_I}/\overline{P}_{n,o}) = 2K[I]_o^{1/2}((1 - x_I)^{1/2} - 1) - \ln\ (1 - x_I)^{1/2} \qquad (5)$$

The corresponding monomer conversion x_M is given by

$$\ln(1 - x_{M,t}) = 2\,K[I]_o^{1/2}\,((1 - x_{I,t})^{1/2} - 1) \qquad (6)$$

Figure 1 shows a set of curves for different values of $[I]_o = k_t k_d / f k_p^2 \underline{a} = 1 / K^2 \underline{a}$.

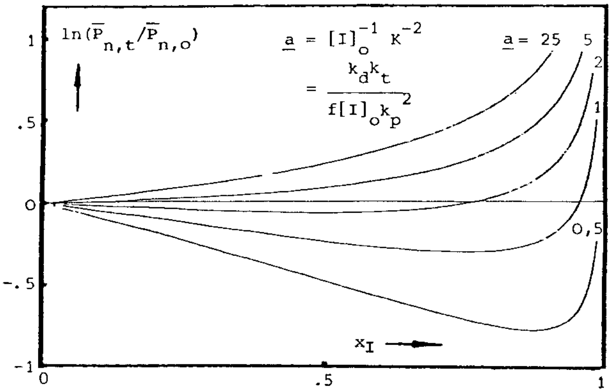

Figure 1:

Optimization curves with respect to polydispersity

For $\underline{a} = 4$ the function has the incline 0 at $x_I = 0$, thus representing one limiting case for optimization of polydispersity at very low initiator conversion. A minimum of cumulative polydispersity $\overline{P}_w/\overline{P}_n$ is reached evidently, when the function $\ln(\overline{P}_{n,x_I}/\overline{P}_{n,o})$ becomes 0 at a given ultimate initiator conversion x_I , since in this case the maximum deviation of $\overline{P}_{n,min}$ from $\overline{P}_{n,max}$, which determines $\overline{P}_w/\overline{P}_n$, has a minimum value. On the other hand, this deviation increases rapidly with $\underline{a}$ decreasing below 1.5. Since the corresponding function crosses the abscissa at nearly .9 initiator conversion - t_{opt} being about 3 initiator half lives, $\overline{P}_{n,min}$ amounting to $.87\,\overline{P}_{n,max}$ and the monomer conversion x_M being about 66 % - this value might be considered as a reasonable limit for practical purposes, especially if one keeps in mind the fact that at very low monomer concentrations the initiator efficiency decreases strongly (9) and other deviations from ideality might become too serious to be neglected. According to data given by TADMOR and BIESENBERGER (10), who calculated polydispersities for high monomer conversions, the cumulative heterogeneity index should still be close to 1.5 in this case ($\underline{a} = 1.5$).

Polymerizations of styrene (33 % by vol. in benzene) have been carried out in two series, with the AIBN conversions 2 and 3.5 half lifetime, respectively. The above calculations have been confirmed in the main, though the optimum value of $\underline{a}$ was found to be somewhat higher than expected, 3 - 4 instead of 1.5 - 2. Figure 2 presents the cumulative polydispersity indices, calculated from GPC, versus initiator concentration, defined by $\underline{a} = 1/[I]_o K^2$.

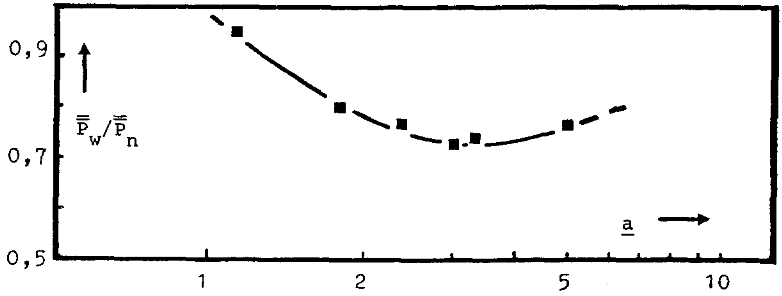

Figure 2:

Cumulative polydispersity indices of polystyrenes from GPC versus AIBN concentration $\underline{a} = 1/[I]_0K^2$

Consequences on block copolymerizations via macroinitiator may be discussed shortly: The molecular weight of the macroinitiator is given, and suitable concentrations of reactants have to be choosen under different aspects, the desired molecular weight of the central block dominantly. Thus, it will be obviously easier to vary the initiator decomposition rate rather than its initial concentration. Rough calculation makes evident that monomers with high values of $k_p/k_t^{1/2}$, such as acrylics, require initiator decomposition within few hours, while the polymerization of less reactive monomers, such as styrene or chloroprene, has to be carried out over several days, when optimization of molecular heterogeneity is asked for.

Finally, the molecular weight of the central block being formed by polymerization via macroinitiator may be discussed. Equation (6) shows that for choosen initiaton conditions monomer conversion x_M is determined. From eq. (7) it becomes evident that the molecular weight is dependent exclusively on initial monomer concentration

$$\bar{P}_{n,t} = [M]_0 x_{M,t} / f\,[I]_0 x_{I,t} \qquad (7)$$

In consequence, it may be concluded that radicalic polymerization steps in block and also in graft copolymerization may be treated in a rigourous stoechiometric way. This fact has remained unconsidered, apparently, in the utmost number of experimental studies reported in this field up to now.

ACKNOWLEDGEMENTS

The authors have to thank cordially Mr. U. WESTPHAL for assistance in setting up the calculator programs. Financial assistance of the BUNDESMINISTERIUM FÜR FORSCHUNG UND TECHNOLOGIE is gratefuly acknowledged.

REFERENCES

1) MEZGER, TH., Dissertation Freiburg i. Br. (1982)
2) FEGER, C., Dissertation Freiburg i. Br. (1981)
3) MEZGER, TH. and CANTOW, H.-J., Angew. Makromol. Chem., in press
4) MEZGER, TH. and CANTOW, H.-J., Makromol. Chem., Rap. Comm., in press
5) FEGER, C. and CANTOW, H.-J., Polymer Bulletin **3**, 407 (1980)
6) TOBOLSKI, A. V., ROGERS, C. E. and BRICKMAN, R. D.
J. Amer. Chem. Soc. **82**, 1277 (1960)
7) NISHIMURA, M., Bull. Chem. Soc. Japan **34**, 1158 (1961)
8) TOBOLSKI, A. V., J. Amer. Chem. Soc. **80**, 5927 (1958)
9) BEVINGTON, J., Transact. Farad. Soc. **51**, 1392 (1955)
10) TADMOR, Z. and BIESENBERGER, J. A.
J. Pol. Sci., Pol. Lett. Ed. **3**, 753 (1965)

Accepted February 15, 1983 C