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Registry No. (*p*-Phenylsulfonylhydroquinone)(1,10-bis(4′-chloroformylphenoxy)decane) (copolymer), 116665-00-0; (*p*-phenylsulfonylhydroquinone)(1,10-bis(4′-chloroformylphenoxy)decane) (SRU), 102961-46-6; (1,4-benzenedicarboxylic acid)(1,2-ethanediol)(4-hydroxybenzoic acid) (copolymer), 25822-54-2.

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Conversion Chemical Heterogeneity of Graft Copolymers Prepared from Macromonomers

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ABSTRACT: The conversion chemical heterogeneity of graft copolymers prepared by statistical copolymerization of an ordinary monomer with a macromonomer has been estimated. Its extent does not depend on the molecular weight of the macromonomer. Consequently, it is comparable with that of common statistical copolymers prepared from two low molecular weight comonomers. The chemical composition distribution is broader the more the monomer reactivity ratio of the ordinary monomer differs from unity.

Introduction

Statistical copolymerization of an ordinary low molecular weight monomer with a macromonomer is an up-to-date and efficient way of preparing graft copolymers.[1] In copolymerizations comprising a macromonomer, two mechanisms producing chemical heterogeneity of products are to be considered, similar to the copolymerization of two ordinary monomers.

The statistical nature of copolymer chain formation gives rise to statistical chemical heterogeneity.[2] With macromonomers, this type of heterogeneity would be significant in typical cases.[3] The conversion heterogeneity originates due to the drift of the monomer–mixture composition (and thus also of the composition of the copolymer molecules formed) depending on the conversion of monomers into copolymer,[4] because both monomers are usually not consumed at equal rates. For a copolymerization including a macromonomer, this effect has been observed experimentally by Niwa et al.[5] and by Tsukahara et al.[6] Both types of chemical heterogeneity occur simultaneously and are superimposed[7] in any practical experiment.

The aim of this contribution is to estimate the extent of chemical heterogeneity due to the conversion in graft copolymers prepared by statistical copolymerization of an ordinary monomer with a macromonomer.

Theory

Chemical Composition Distribution (CCD). A typical feature of a statistical copolymerization which includes a macromonomer as one of the monomers is the low molar content of the macromonomer in the reaction mixture. If we denote the molar concentration of the ordinary monomer in the mixture as [A], and that of a macromonomer [M], then for $[A] \gg [M]$ the classical copolymerization equation reduces,[1] for the monomer reactivity ratios not too different from unity, to

$$\frac{d[A]}{d[M]} = r_A \frac{[A]}{[M]} \qquad (1)$$

The chemical composition of the copolymer is thus controlled, apart from the concentration of monomers, only by the monomer reactivity ratio r_A of the low molecular weight monomer. This parameter is assumed to be, similar to the classical copolymerization of two comonomers, independent of conversion. Integration of eq 1 yields

$$\frac{[A]}{[A]_0} = \left(\frac{[M]}{[M]_0}\right)^{r_A} \qquad (2)$$

The subscript 0 denotes the value of a quantity in the starting mixture, i.e., at zero conversion.

The relation between the composition of the monomer mixture, f, in terms of the mole fraction of monomer A

$$f = \frac{[A]}{[A] + [M]} \qquad (3)$$

and the mole conversion of monomers to copolymer, ψ_m

$$\psi_m = 1 - \frac{[A] + [M]}{[A]_0 + [M]_0} \qquad (4)$$

is obtained

$$\psi_m = 1 - \left(\frac{f}{f_0}\right)^{-(\beta+1)}\left(\frac{1-f}{1-f_0}\right)^{\beta} \qquad (5)$$

after rearrangement of eq 2. The parameter β is defined as $\beta = r_A/(1 - r_A)$.

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Copolymerization eq 1 can be rewritten to relate the instantaneous copolymer composition, F, in terms of the mole fraction of constitutional units A to the composition of the monomer mixture, f

$$F = \frac{r_A f}{(r_A - 1)f + 1} \tag{6}$$

By use of eq 5 and 6, the conversion can be expressed as a function of copolymer composition, $\psi_m(F)$. After normalization by the final conversion $\psi_m^* \leq 1$, the ratio $\psi_m(F)/\psi_m^*$ has the meaning[4] of the integral CCD, because it gives the fraction of copolymer macromolecules with composition less than or equal to F (if F decreases with conversion, it has to be formally replaced by $1 - F$). The CCD of this type applies exactly to a copolymer of infinite molecular weight when the statistical chemical heterogeneity does not manifest itself. For copolymers of a finite molecular weight, the additional broadening of the CCD due to the statistical heterogeneity should be taken into account.

Chemical Composition Distribution in Terms of Weight Fractions. In practical applications, it may be an advantage to describe the course of a copolymerization by variables defined on a weight basis, i.e., in terms of the weight conversion of monomers, ψ; weight fraction of monomeric units A in the copolymer, x; and the weight fraction of monomer A in the monomer mixture, y. The molar and weight compositions of the copolymer, F and x, and of the monomer mixture, f and y, can be related by

$$F = \frac{x}{(1 - t)x + t} \tag{7}$$

$$f = \frac{y}{(1 - t)y + t} \tag{8}$$

where $t = M_{0A}/M_{0M}$ is the ratio of molecular weights of monomers. From the material balance, the general relation between the mole and weight conversion is obtained:

$$\begin{aligned}(1 - \psi) &= \frac{1 - (1 - t)f}{1 - (1 - t)f_0}(1 - \psi_m) \\ &= \frac{(1 - t)y_0 + t}{(1 - t)y + t}(1 - \psi_m)\end{aligned} \tag{9}$$

The subscript 0 again refers to the starting composition of the mixture of monomers.

Introducing the weight composition y in eq 5 and using eq 9, we obtain

$$\psi = 1 - \left(\frac{y}{y_0}\right)^{-(\beta+1)}\left(\frac{1 - y}{1 - y_0}\right)^{\beta} \tag{10}$$

i.e., a result in the same formal layout as in eq 5. Similarly, the copolymerization eq 6 can be rewritten as

$$x = \frac{r_A y}{(r_A - 1)y + 1} \tag{11}$$

It should be noticed that eq 10 and 11 do not include the parameter t. The last two equations allow us to calculate the integral CCD, $I_w(x) = \psi(x)/\psi^*$, where $\psi^* \leq 1$ is the final weight conversion of copolymerization.

The differential weight CCD is obtained by differentiation of the integral CCD

$$\begin{aligned}W(x) &= \frac{dI_w(x)}{dx} = \frac{1}{\psi^*}\left|\frac{d\psi(x)/dy}{dx/dy}\right| \\ &= \left|\frac{(\psi - 1)}{\psi^*}\,\frac{\beta(\beta + 1)}{x(1 - x)(\beta + x)}\right|\end{aligned} \tag{12}$$

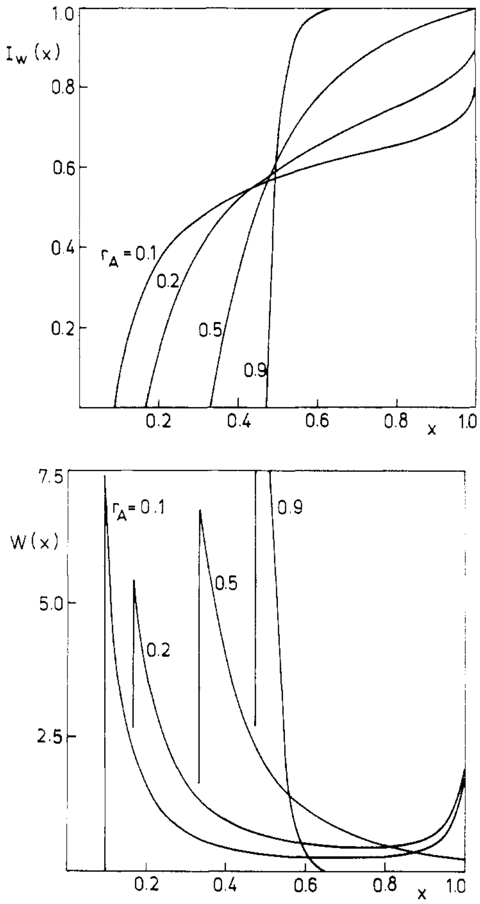

Figure 1. (a, Top) Integral weight CCD, $I_w(x)$, and (b, bottom) differential weight CCD, $W(x)$, for statistical copolymers of an ordinary monomer A with a macromonomer M for different monomer reactivity ratios r_A. x is the chemical composition of copolymer macromolecules in terms of weight fractions of A. The starting composition of monomer mixture is $y_0 = 0.5$ (i.e., 50 wt % of A). Complete conversion of monomers, $\psi^* = 1$; then, $I_w(x)$ is numerically equal to the weight conversion of monomers, ψ.

In a practical computation of the CCD, the composition of the monomer mixture y is varied from y_0 to either zero or unity, and the corresponding conversion ψ is evaluated from eq 10. The relevant range of y values is that which yields physically meaningful conversions ψ, i.e., $0 \leq \psi \leq \psi^*$. For these values of y, the instantaneous copolymer composition x is calculated from eq 11. The plot of ψ/ψ^* against copolymer composition x represents the desired integral CCD. The differential CCD is similarly obtained with the help of eq 12.

Results and Discussion

Although the relations between the mole and weight fraction of comonomers (eq 7 and 8) depend on molecular weights of comonomers through the parameter $t = M_{0A}/M_{0M}$, this parameter enters neither the conversion–composition dependence in terms of weight fractions (eq 10) nor the corresponding form of the copolymerization equation (eq 11). Consequently, the extent of chemical heterogeneity of copolymers, described by the CCD, is not affected by the molecular weight of the macromonomer or by the potential nonuniformity of the macromonomer in molecular weight. The copolymerization of a monomer with a macromonomer is formally described by the same equations as a binary copolymerization of two monomers, for which the product of their monomer reactivity ratios is $r_A r_B = 1$.

Model calculations show that the more the ratio r_A differs from unity the broader is the CCD that results

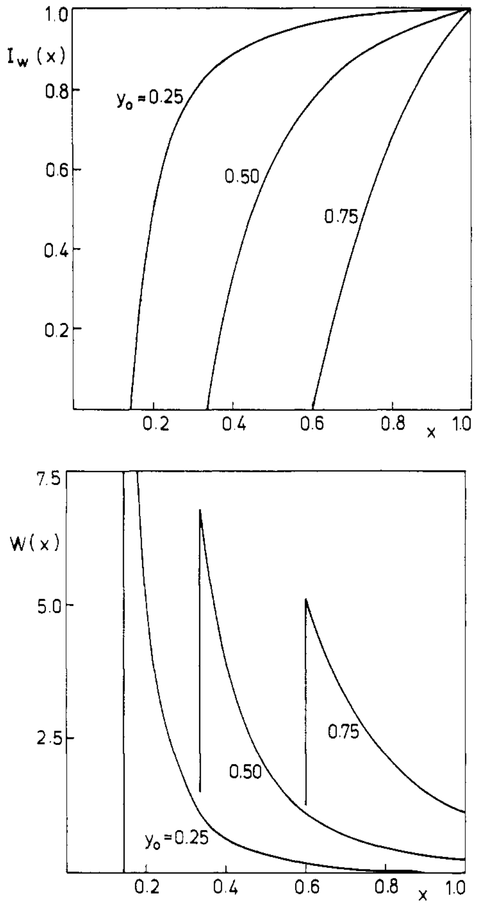

Figure 2. (a, Top) Integral weight CCD, $I_w(x)$, and (b, bottom) differential weight CCD, $W(x)$, for statistical copolymerization of an ordinary monomer A with a macromonomer M for different compositions of the starting mixture of monomers, y_0, in terms of the weight fraction of monomer A. $r_A = 0.5$; cf. also Figure 1.

(Figure 1). For example, for equal weights of comonomers in the starting mixture (Figure 1), the copolymer prepared up to 50 wt % conversion will contain macromolecules differing by 25 wt % in the content of the macromonomer for $r_A = 0.1$, 21 wt % for $r_A = 0.2$, 11 wt % for $r_A = 0.5$, and 2 wt % for $r_A = 0.9$ (Figure 1a). At copolymerizations carried out to higher conversion, these differences are still higher (Figure 1a). A figure identical with Figure 1 could be drawn for $r_A = 10$, 5, 2, and 1.1, if x had the meaning of weight fraction of the macromonomer in the copolymer. For low r_A values (e.g., for $r_A = 0.1$ and 0.2 in Figure 1a), the macromonomer is totally depleted from the reaction mixture before complete conversion is reached. A homopolymer from the low molecular weight monomer A is formed in the last stages of polymerization.

The starting composition of the monomer mixture, y_0, affects the chemical heterogeneity of copolymers in such a way that for $r_A < 1$ the CCD broadens as the weight fraction y_0 of the ordinary monomer A is decreased (Figure 2). The opposite is true for $r_A > 1$.

Conclusions

In copolymers prepared by statistical copolymerization involving a macromonomer, the conversion chemical heterogeneity may be significant. It is expected to be high if the monomer reactivity ratio of the ordinary monomer substantially differs from unity. Such a situation is especially likely to occur when the structure of the macromonomer end group strongly differs from that of the low molecular weight comonomer.[6]

The extent of conversion chemical heterogeneity is independent of molecular weight of the macromonomer and is determined only by the weight fraction of the macromonomer in the starting mixture and by conversion.

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Comparison of Dynamic Rotational Isomeric State Results with Previous Expressions for Local Chain Motion

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ABSTRACT: The dynamic rotational isomeric states model is used to calculate the conformational (CACF) and first and second orientational (OACF) autocorrelation functions for polyethylene. Various sequence lengths and directions in the chain are considered. The CACFs are compared with Brownian simulation results of Weber and Helfand. Results of calculations on OACFs are analyzed by using the expressions proposed for local chain dynamics by Williams–Watts, Jones–Stockmayer, Bendler–Yaris, and Hall–Helfand. The relationship between the correlation times associated with the first and second OACFs is examined.

Introduction

It is now widely accepted that, among various processes contributing to chain relaxation on a local level, the torsional motion of skeletal bonds, leading to transitions between isomeric states, plays a dominant role.

A quantitative measure of local orientational motions is the orientational autocorrelation function (OACF), reflecting the transient behavior of one or more vectorial

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