Molecular Weight Distribution of a Novel Condensation Polymerization. Comparison with Theory

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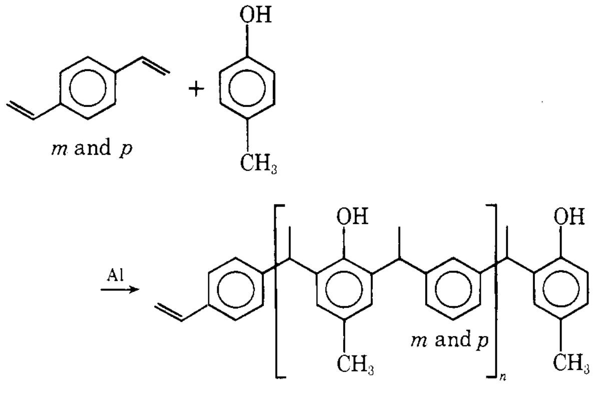
ABSTRACT: The polymerization of divinylbenzene and *p*-cresol has been followed by gel permeation chromatography. The production of low molecular weight oligomers in the early stages of the reaction is characteristic of a typical condensation polymerization. An analysis of the relative amounts of *p*-cresol, dimer, and trimer, however, shows that the molecular weight distribution is not that of the "most probable" distribution. In addition, evidence from GC/MS suggests that all functional groups are not equally reactive. These findings are discussed in terms of a theoretical treatment of nonrandom polymerization. Incorporating the assumption that each ortho site on *p*-cresol is between two and four times as reactive as that on monosubstituted cresol provides a calculated distribution in better agreement with the data. A modified extent of reaction parameter, p^*, is suggested for direct comparison of theory and experiment.

The polymerization of divinylbenzene (DVB) and *p*-cresol (reaction 1) is an example of the aluminum-catalyzed ortho alkylation of phenols.[1] Because the Al must apparently "activate" the phenol via coordination, it was not obvious, a priori, whether the resulting molecular weight distribution would correspond to that of an addition polymerization or that of a classical polycondensation. Examination of the reaction products, however, reveals the initial formation of low molecular weight oligomers with subsequent conversion to species of higher and higher molecular weight.[2] This observation is consistent with reactivity distributed among all functional groups, i.e., a polycondensation, and not limited to the activated growing end of a polymer chain.



(1)

Compounds of the class typified by the product of eq 1 are of interest as polymeric antioxidants.[3,4] In order to obtain the full benefit of their polymeric character, whether it be nonvolatility or biological nonabsorbability, it is necessary to limit the concentration of the low molecular weight components of these materials.[5] In the course of the development of such materials, the effects of alterations in synthesis parameters upon the molecular weight distribution were predicted from calculations based on theoretical treatments of condensation polymerizations. To determine how accurately these theoretical methods predict the distribution of low molecular weight components in this novel condensation polymerization, we have investigated the products of such a reaction by means of gel permeation chromatography (GPC).

Experimental Section

Materials. Commercial (Dow) divinylbenzene (DVB) containing 75% DVB and 25% ethylvinylbenzene (EVB) was purified via the DVB·CuCl complex[6] and distilled. NMR and gas chromatography showed the product to contain 95% DVB (62% meta and 38% para isomers) and 5% EVB. All other materials were reagent grade and were used without further purification.

Polymerization. Al (0.0261 g) and *p*-cresol (2.148 g) were heated at 135 °C in a small amount of toluene for 20 min and then cooled. DVB (2.769 g, including 5% EVB) and toluene (13 g) were added, and the mixture was heated under N_2 to 114 ± 1 °C. Aliquots (0.25 mL) were taken periodically from the homogeneous mixture for GPC.

Analyses. Gel permeation chromatography (GPC) was performed on three 500 Å μStyragel columns (Waters Associates) in THF with detection by absorbance at 280 nm and by differential refractive index. Typical chromatograms are shown in Figure 1.

The concentrations of monomer, dimer, and trimer were determined from the areas under the GPC chromatograms in conjunction with calibration curves obtained by direct injection of standards. Dimer and trimer standards were prepared by GPC fractionation of several pooled aliquots from the midrange of the polymerization. Combined GC/MS confirmed assignment of the dimer and trimer peaks. The calibration curves were not corrected for solvent content because of the small amounts of material available, but solvent content of similarly isolated material is typically below 10%.

Results and Discussion

The concentration of cresol in the polymerization mixture is plotted as a function of time in Figure 2. The induction period may be due to the slow initial formation of aluminum cresoxide. The kinetics of the disappearance of monomer do not fit any simple analysis. In the usual case, the disappearance of unreacted cresol would be proportional to cresol concentration and total vinyl concentration. Both these concentrations may be expressed as functions of the extent of reaction (p), which is simply the fraction of limiting functional group consumed. For perfect stoichiometry,

$$[\text{cresol}] = [\text{cresol}]_0(1-p)^2$$

$$\begin{aligned}[\text{total vinyl groups}] &= [\text{total vinyl groups}]_0(1-p)\\ &= 2[\text{cresol}]_0(1-p)\end{aligned}$$

where the subscript 0 indicates initial concentration. Thus,

$$\begin{aligned}\frac{-\mathrm{d}[\text{cresol}]}{\mathrm{d}t} &= k[\text{cresol}][\text{total vinyl groups}]\\ &= k'(1-p)^3\\ &= k''[\text{cresol}]^{3/2}\end{aligned}$$

The disappearance of cresol would therefore be $^3\!/_2$ order in cresol concentration. (An analysis of the disappearance of total functional groups would, of course, lead to the more familiar second-order dependence.) In the present case, however, monomer concentration over the entire range is best fit by a $^1\!/_2$ order plot. Because molecular weight distribution theories describe the interrelation between species of various molecular weight with no direct dependence on time, the question of kinetics was not pursued.

The simplest theory for the molecular weight distribution of condensation polymers is that developed by Flory,[7] Schultz,[8] Stockmayer,[9] and others, based upon the principle

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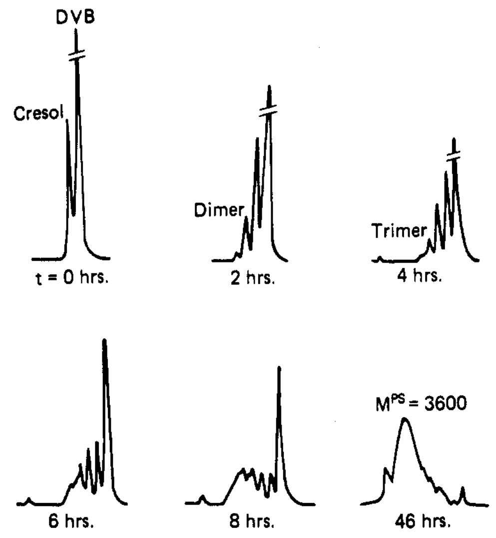

Figure 1. GPC chromatograms of DVB–cresol reaction aliquots.

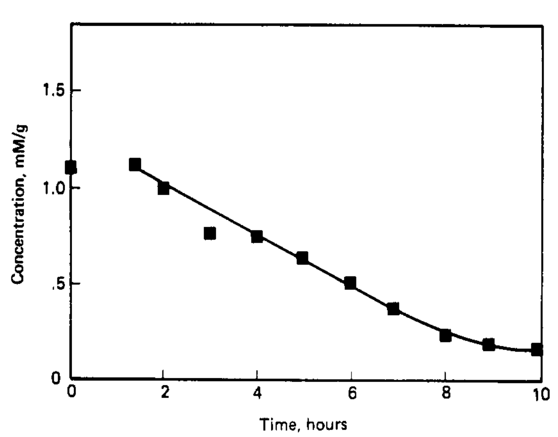

Figure 2. Concentration of *p*-cresol as a function of time.

of equal reactivity. It is assumed that at any given stage of the polymerization all functional groups are equally reactive regardless of the size of the molecule to which they are attached and that no intramolecular cyclization occurs. The molecular weight distribution consequently predicted is known as the "most probable" distribution.

In order to compare the experimentally determined molecular weight distribution (MWD) with that predicted from theoretical models, it is necessary to express both distributions as a function of the extent of reaction. This quantity is typically measured by end-group analysis of polycondensation mixtures, but no such direct chemical method applies for the products of this reaction. The redox potential of the phenolic moiety, which provides the polymer with antioxidant properties, interferes with methods for titration of the unreacted vinyl groups. Indirect techniques, such as quantitation of vinyl protons by NMR, are limited by poor resolution. We chose, therefore, to relate the extent of reaction to the weight fraction, w_c, of remaining comonomer (*p*-cresol) as given by the most probable distribution,

$$p^* = 1 - (w_c/w_{c0})^{1/2} \qquad (2)$$

(where w_{c0} is the initial weight fraction of *p*-cresol). We may then compare experimental and predicted values for dimer and trimer levels as a function of p^*.

In Figure 3 the dependence of dimer and trimer concentrations on p is compared to that corresponding to the most probable distribution.[10] There are two striking discrepancies:

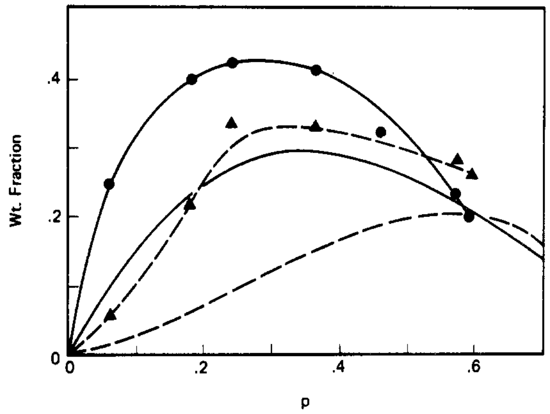

Figure 3. Observed concentration of dimer (-●-) and trimer (-▲-) and concentration of dimer (—) and trimer (- - -) for a "most probable" distribution.

(a) the amounts of dimer and trimer are larger than the calculated value, and (b) the maximum concentrations of dimer and trimer occur at lower values of p. Because the extent of reaction was calculated from cresol concentration, observation (b), in fact, reflects the rate of production of dimer and trimer vs. the consumption of monomer.

An explanation of these findings was suggested by results from gas chromatography/mass spectroscopy (GC/MS) data for dimer and trimer fractions obtained by preparative GPC. Although the dimer fraction contained both expected molecules (DVB–cresol and EVB–cresol), the trimer fraction was found to be predominantly phenol terminated (cresol–DVB–cresol) and not "vinyl" terminated (DVB–cresol–DVB, etc.). In contrast, a trimer fraction isolated from a similar polymerization (using a mixture of phenolic comonomers) at *high conversion* contained predominantly DVB–phenol–EVB and EVB–phenol–EVB species and little phenol-terminated trimer.

These observations suggest that each of the two ortho sites of *p*-cresol is considerably more reactive than that of its mono-substituted product. This could be due to differences in coordinating power for Al^{3+}. Such unequal reactivity is shown in Scheme I, where k_a refers to the reactivity of a single *p*-cresol site. Trimer can be formed in only two ways (neglecting depolymerization):[11] If $k_a \gg k_b$, most of the trimer formed initially, at equal concentration of the two comonomers, will be cresol terminated. As the reaction proceeds,

Scheme I

$$\text{DVB–cresol} + \text{cresol} \xrightarrow{k_a} \text{cresol–DVB–cresol}$$

$$\text{DVB–cresol} + \text{DVB} \xrightarrow{k_b} \text{DVB–cresol–DVB}$$

cresol will be depleted because of its higher reactivity, and the predominant form of trimer produced at high conversion will be vinyl terminated. Moreover, the maximum concentration of dimer and trimer species should be higher than for the case of equal reactivity, because of the increase in the ratio of the rate of formation to the rate of consumption.[12] Note, however, that the true extent of reaction and monomer content are no longer related according to eq 2. However, p^* remains a measure of the progress of the reaction and can still be used as a parameter linking calculated and observed distributions.

Some differences in reactivity might also be expected for DVB. If DVB differed significantly in reactivity from half-reacted DVB, it would similarly differ from EVB. In polymerizations with considerably higher EVB concentrations than employed here, we find no differential incorporation of

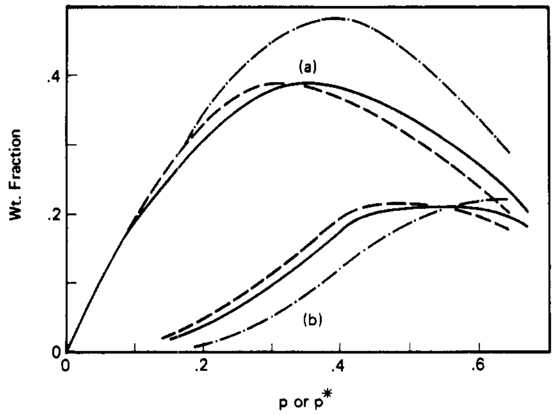

Figure 4. Concentration of (a) dimer and (b) trimer calculated according to Kuhn (ref 12). Plotted against true extent of reaction for $\mu = 2$ (- - -) and against p^* for $\mu = 2$ (—) and $\mu = 4$ (- · · -)

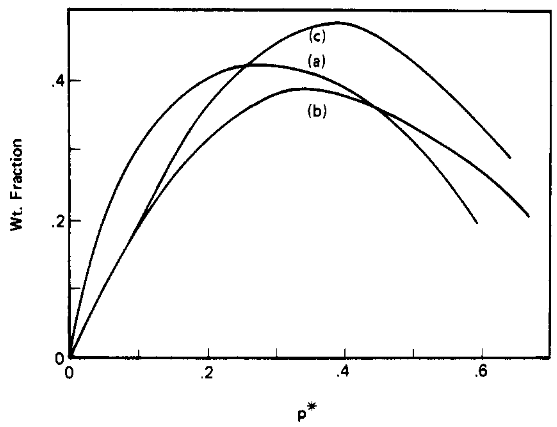

Figure 5. Concentration of dimer vs. p^*: (a) observed, (b) calculated for $\mu = 2$, (c) calculated for $\mu = 4$.

EVB. We expect other resonance and inductive effects, such as those for meta and para isomers, to be small compared with the differences discussed here for p-cresol.

This modification to the principle of equal reactivity has been treated by several authors. Kuhn[12] examined the degradation of cellulose chains in which terminal bonds are cleaved more rapidly than internal bonds. The reverse of this process is formally equivalent to a polymerization with free monomer reacting more slowly than half-reacted monomer; the same molecular weight distribution would be predicted in either direction.[13] More recently, Amemiya[14] has examined the same situation in great detail, but the results are extremely complex. "Unequal reactivity" in the forward (polymerization) direction has been examined from equilibrium considerations by Challa,[15] but only for A–B type monomers. The case of two comonomers (AA and BB) has been treated from a kinetic point of view in unpublished work by J. J. Hermans cited and developed by Peebles.[16]

The equations (see Appendix) provided by Challa and Peebles, and an adaption of those by Kuhn, were all solved numerically to yield monomer content and hence p^* as a function of the true extent of reaction for various values of $\mu \equiv k_a/k_b$. The three treatments agreed closely. Kuhn's equations, however, were much more tractable for dimer and trimer and were solved for various ratios of end-group reactivity to internal reactivity. For the case of one comonomer with two or four times the reactivity of all other species, the concentrations of dimer and trimer are plotted in Figure 4 against the true extent of reaction p and against p^* calculated from eq 2. The latter plots permit direct comparison with our experimental results, as is shown for dimer in Figure 5. Although the Kuhn distribution provides better agreement than the most probable distribution for the amount of dimer, it fails to do so for the position of the concentration maximum. Similarly, the agreement with observed trimer concentration is better for the Kuhn distribution, but the discrepancy in predicted and observed values is considerably greater than for dimer.

In summary, the low-conversion molecular weight distribution arising from the condensation of divinylbenzene and p-cresol is apparently different from that predicted on the basis of the principle of equal reactivity. GC/MS data provide evidence for elevated reactivity of free p-cresol. Theoretical predictions incorporating such unequal reactivity provide better, but still imperfect, agreement with results.

Acknowledgments. We gratefully acknowledge helpful discussions with Dr. James Dale, who developed the polymerization, and with Professor Paul Flory. We also thank Dr. Leonard Bunes for purifying the DVB and Mr. James Starr for writing the computer program.

Appendix. Molecular Weight Distribution Equations

Kuhn[12] has provided expressions for the molecular weight distribution arising from the cleavage of infinitely long chains, where the rate of end-group cleavage k_2 differs from that of internal cleavage k_1. If $\beta = (k_2/k_1) - 1$, α is equal to the degree of cleavage, and w_i is the weight fraction of $i$mer:

$$1 - \alpha = \exp(-k_2 t)\exp[\beta(1 - \exp(-k_1 t))] \tag{A1}$$

$$w_1 = 1 - (1 - \alpha)(2 - e^{-k_1 t}) \tag{A2}$$

$$w_2 = 2(1 - \alpha)(1 - e^{-k_1 t})^2 \tag{A3}$$

$$w_3 = 3(1 - \alpha)(1 - e^{-k_1 t})^2 e^{-k_1 t} \tag{A4}$$

We have simplified eq A2–4 by substituting $(1 - \alpha)$ for the expression on the right side of eq A1.

The cleavage of infinite chains may be viewed[13] as the reverse of polymerization with $(1 - \alpha)$ corresponding to the extent of reaction p. We may apply the same equation with $t = \infty$ corresponding to $p = 0$ (i.e., complete cleavage of Kuhn's chains) and $t = 0$ corresponding to $p = 1$. End-group cleavage then corresponds to reaction of a free monomer and internal cleavage to the (reverse) reaction of half-reacted monomer. We note, however, that increased reactivity of free monomer corresponds to *decreased* end-group cleavage. Hence, $\mu \equiv k_a/k_b = (k_2/k_1)^{-1}$. Since we are interested in p-cresol rather than total monomer, we rewrite eq A2 as

$$w_c = w_{c0}\{1 - (1 - \alpha)(2 - e^{-k_1 t})\} \tag{A2$'$}$$

and solve these equations parametrically for various values of $k_1 t$. From w_c we calculate p^* by eq 2 and obtain the curves in Figure 4.

We also obtained solutions for w_c, and hence p^*, from two other sources. Challa[15] found the following expressions, which we have recast in our notation, from equilibrium considerations:

$$\frac{1}{p} = 1 + (1 - r) + \frac{(1 - r)^2}{\mu r} \tag{A5}$$

$$\frac{1}{f} = (1 - p) + \frac{(1 - p)}{(1 - r)} r\mu \tag{A6}$$

$$w_1/w_{1_0} = f(1 - p)^2 \tag{A7}$$

We have set $\mu = K_1/K_0$, the ratio of the equilibrium constants for polymerization with unreacted and half-reacted monomer. The parameter w_1 is the weight fraction of the single AB type monomer, while f is the ratio of actual monomer content to that predicted from equal reactivity. We solve these equations sequentially to find w_1 and p^* as a function of p.

The equations of Hermans, provided by Pebbles,[16] correspond to a more general case of our problem. Assuming perfect stoichiometry and noting that Peeble's variable $Q = 2w_{c0}(1 - p)$, the results reduce to:

$$(1 - p) = \frac{1}{2\mu - 1}\left\{\mu\left[\frac{w_c}{w_{c0}}\right]^{1/2\mu} + (\mu - 1)\left[\frac{w_c}{w_{c0}}\right]\right\}$$

This expression was also used to find the relationship between p and p^* for various values of μ.[17]

References and Notes

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Effect of Molecular Weight On Excimer Formation of Polystyrenes in Solution

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ABSTRACT: The fluorescence quenching of monomer and excimer emission bands of polystyrenes in 1,2-dichloroethane solution by oxygen was measured under steady-state and non-steady-state conditions as a function of molecular weight. These measurements permitted calculation of such parameters as the rate constants for excimer formation, dissociation, radiative and nonradiative deactivation processes, and other parameters such as the quenching constant for the monomer emission band and the migration coefficient. These parameters showed molecular weight dependence below 1.0×10^4 but were constant above it. These phenomena revealed that the intramolecular interaction of adjacent chromophores in the polymer chains of high molecular weight polystyrenes was very effective and favored excimer formation, but the interaction in low molecular weight polystyrenes was not so effective for excimer formation because of the isolating tendency of phenyl rings.

There have been many studies made of the intramolecular excimer formation of 1,3-diphenylpropane, 1,3,5-triphenylpentane, and polymers containing aromatic chromophores.[1-5] The "$n = 3$" rule of Hirayama reveals that excimers can be formed between two chromophores separated by three carbon atoms along the alkane chain. The preferred spatial alignment of a pair of chromophores for excimer formation is assumed to be a parallel sandwich type, but strict adherence to this conformational orientation is not necessary.[6,7]

It has been shown that intramolecular excimer formation for polymers is controlled by both configuration and conformation in a polymer chain.[8,9] In addition, the intramolecular dynamics of macromolecules is important for the transient phenomena of excimer formation in the excited state.

The dynamic processes for macromolecules in solution, especially at high frequencies, have been probed by using such methods as dielectric dispersion, NMR, EPR, depolarized Raman and Rayleigh spectroscopy, and fluorescence depolarization.[10-15] The relaxation time obtained from the dynamic processes agrees well with the time of excimer formation for polystyrene of molecular weight above 1.0×10^4.

This paper reports studies of the molecular weight effect on excimer formation of polystyrenes by using the rate parameters of excimer formation calculated from fluorescence quenching as a function of molecular weight measured under steady-state and non-steady-state conditions.

Experimental Section

Materials. The polystyrene samples were monodispersed standard polymers (Pressure Chem. Co.) of molecular weight 600, 900, 2.1×10^3, 4.0×10^3, 1.0×10^4, 3.7×10^4, 1.1×10^5, and 3.9×10^5.

The 1,2-dichloroethane solvent (DCE) used for fluorescence measurements was purified by the fractional distillation procedure prescribed for the guaranteed reagent grade.[16]

Measurements. Fluorescence spectra were measured with a MPF-4 type Hitachi fluorescence spectrophotometer. Fluorescence measurements were conducted at an excitation frequency of 255 nm with an emission slit width of 4 nm and an excitation slit width of 8 nm. Conditions were the same for all measurements. The concentration of all polymer solutions was 3 mmol/L (chromophore unit).

The relative fluorescence quantum yields of the polymers were determined from the area of the fluorescence spectra relative to the area of the spectra for standard anthracene solution in aerated alcohol, assuming that its quantum yield was 0.23.[17]

The quenching measurements were carried out after confirming that the dissolved air in the sample solution had been completely replaced with gaseous nitrogen or oxygen, which were bubbled through the solution.[18] This confirmation was obtained from the fact that after aeration the fluorescence intensity was constant.

The oxygen concentration in an aerated DCE solvent at room temperature was determined by gas chromatography, in which the separation of oxygen was carried out on molecular sieve column (13-X, Nishio Kogyo). The oxygen concentration in the aerated and oxygenated DCE was determined to be 2.3×10^{-3} mol/L and 12.9×10^{-3} mol/L, respectively.

The effect of temperature on fluorescence intensity was measured between −15 and 60 °C. Temperature regulation was accomplished

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