Table I
Monomer Reactivity Ratios for Reactions of Styrene Radicals with Different Penultimate Groups with Oxygen

	C&B[2]	M[1]
r for –S–S·	5.2×10^{-6}	4.4×10^{-8}
r for –O_2–S·	3×10^{-6}	1.8×10^{-6} to 3.3×10^{-7}
r for –O–S·	6.4×10^{-6}	8.0×10^{-7} preferred

of rejection of the low molecular weight, higher oxygen copolymers by C&B.

Monomer Reactivity Ratios

The next point for discussion is the values of the monomer reactivity ratios (MRR, r) for radicals ending in a styrene unit, i.e., the ratio of the rate constants for the reaction of this radical with styrene monomer and with oxygen, respectively. M-4.5 shows that this ratio is constant from 760 down to about 15 torr of oxygen but then decreases sharply, possibly becoming nearly constant again below 2 torr. This change in MRR was accounted for (M-4.5) by postulating that it had two values, one for a styrene radical with a penultimate peroxide group (predominating at high oxygen pressures) and one for a styrene with a penultimate styrene unit (predominating at very low oxygen pressures). The MRR's were estimated by three slightly different methods; the results are in Table I. All methods gave the same r_{SS}, but r_{O_2S} varied considerably. The simplest interpretation of this difference is that the –MM· radical reacts faster than the –O_2M· radical with oxygen, a difference consistent with several other copolymerization and chain transfer reactions (M-4.5). Bamford and Basahel[3] recently reported a similar effect of penultimate methyl acrylate units in chain transfer of styrene with CBr_4. Their paper appears to establish the existence of a penultimate effect without any need for involving complexing.

In determining MRR's, the M treatment includes the benzaldehyde and styrene oxide formed as having been incorporated temporarily in the growing polymer radical. Although some account was taken of the presence of ether and excess methylene groups in the copolymer, the MRR calculations are based mostly on the total oxygen in the copolymer, as if the latter contained only C_8H_8 and O_2 units. The C&B treatment neglects the contributions of all the methanol-soluble materials but calculates MRR's for styrene units with penultimate styrene, –O_2–, and –O– units. However, the MRR's based on their copolymer made at 15 torr do not accurately predict the sequence distribution in the copolymer made at 1 atm of oxygen. Table I shows that M's upper limit of r for –O_2–S· approaches that of C&B, but that the values for r_{SS}. differ by about 100-fold. We conclude that there is probably a substantial penultimate effect as reported by M, but his failure to resolve effects of –O–S· and –O_2–S· radicals render his results quantitatively unsatisfactory. The C&B results are based on reprecipitated polymer and therefore neglect more than half of the styrene that was temporarily incorporated in growing radicals.

End Groups

We agree that most of the polyperoxide molecules formed at 1 atm of oxygen are the result of chain transfer. M-5 indicates that 20–25 molecules of polyperoxide are formed per AIBN decomposed, i.e., 16–21 per initiating radical at 60% efficiency of initiation, in good agreement with the C&B finding of one AIBN fragment per 16 chains. Although C&B have made a new contribution on end groups, their conclusions (p 174) leave unsolved problems. The most serious of these is their finding of about 0.67 benzoyl (Bz) groups per chain, in addition to about 0.33 benzoylperoxy (BzO_2·) groups per chain.

We can account for only 0.14 Bz groups per chain to balance the –CH_2–CHPh–OH group formed in the Russell termination mechanism. We agree that benzaldehyde, formed from the polyperoxide radical, accounts for chain transfer after a moderate conversion, but it cannot contribute to chain transfer in the earliest stages of the oxidation. Further, this transfer would produce BzO_2· end groups at the beginning of the next chain. The excess Bz groups might come from decomposition of –CH_2–CHPh–O_2H end groups. An obvious source of these groups is transfer of peroxy radical with benzaldehyde, but then formation of additional BzO_2 groups would be required. We can hardly propose oxidation of –CH_2–CHPh–OH or more benzoyl groups by chain termination; we already have too much termination for the AIBN end fragments found. Additional HO_2· end groups could be formed by reaction 42 in M-5, where a terminal styrene radical, instead of adding oxygen, donates an α-hydrogen atom to the oxygen, leaving a terminal –CH═CHPh group (not considered by C&B) and an initiating HO_2· group. However, decomposition of this hydroperoxide group would not give the required Bz group. Probably the end group and chain transfer problems cannot be solved without consideration of all the end groups, most of which may be in the lost low polymer.

Conclusions

This note has reviewed the present status of problems associated with the presence of excess methylene groups, estimation of monomer reactivity ratios, and end groups in the oxidation of styrene to polyperoxide. Needs for further work to resolve these problems are indicated. We add here a new explanation for the formation of benzaldehyde and formaldehyde in the pressure-independent cleavage of polyperoxide at high oxygen pressures. Nonterminating interactions of peroxy radicals have been well established[4,5] since the Mayo papers were written. They now appear to offer the best explanations for the formation of aldehydes from styrene and for acetophenone from α-methylstyrene at high oxygen pressures:

$$2\ \text{-S-O}_2\text{-S-O}_2\cdot \rightarrow 2\ \text{-S-O}_2\text{-S-O}\cdot + \text{O}_2$$

The resulting alkoxy radicals then decompose at once to the carbonyl compounds.

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Continuous Method To Determine Solubility in Polymer Blends

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Introduction

Polymer blends have drawn considerable attention in recent years because combining existing polymers may give

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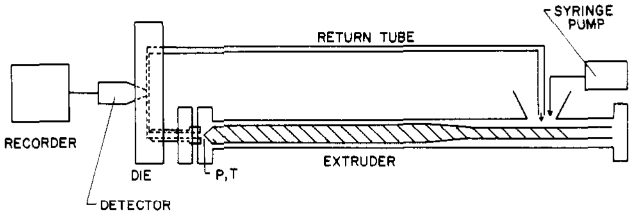

Figure 1. Arrangement for continuous melt titration.

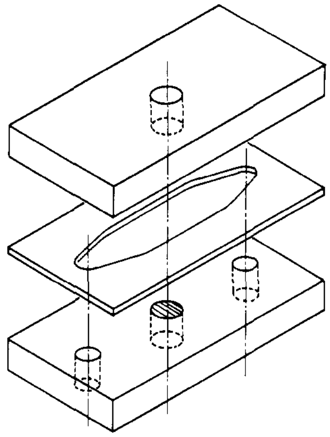

Figure 2. Exploded view of die.

rise to materials having properties superior to the individual components.[1-3] Additionally, the manufacture of a new polymer can often be avoided by blending existing polymers, an economically favorable circumstance. From a scientific viewpoint, the phase behavior of blends is likely to provide valuable clues about the interactions between unlike macromolecules. To provide a basis for this understanding, it is important to know to what extent the two polymers are mutually soluble, that is, at what composition phase separation occurs.

A technique for measuring the miscibility in two-component polymer systems was reported earlier[4] in which the addition of one component to another was done progressively on a two-roll mill and the presence of two phases was detected by light scattering on aliquots removed during the addition process. In this note we report on a modified method wherein the scattering intensity is monitored continuously. Several other advantages accrue, namely, the avoidance of dust contamination and complete control of the system's temperature and pressure.[5]

Experimental Technique

A schematic drawing of the experimental setup is given in Figure 1. A known quantity of the first, or base polymer, is fed to the extruder. The melt is extruded into a slit base, polymer is to a recycle tube which returns it to the hopper of the extruder. Thus, a fixed amount of the first polymer is circulated in the system. The second polymer, dissolved in a volatile solvent, is added continuously from a syringe pump to the hopper of the extruder; the presence of a second phase in the mixture is detected by light scattering, using a special die and optical system.

An isometric view of the die is given in Figure 2. The bottom half has two 1.27-cm holes; one is the inlet for the polymer from the extruder, and the other is the outlet for the return tube. At the center of the die a 2.54-cm plug is inserted on which a glass mirror is fastened from the inside. The plug can be adjusted so that the mirror surface is level with the metal surface. The top half of the die has a 2.54-cm hole in the center. A metal insert with a conical opening is made to fit in this hole, and a glass window is fastened to the insert from inside. For fastening, a high-temperature silicone glue is used, which also acts as a gasket between the glass and metal surface. The position of this insert can also be adjusted such that the glass window is level with the die surface. An aluminum shim, 0.32-cm thick, separates the two halves, forming a gap in the die for the polymer to flow through. To avoid any holdup in the die, the boundary of the shim which comes in contact with the polymer is given a streamlined shape.

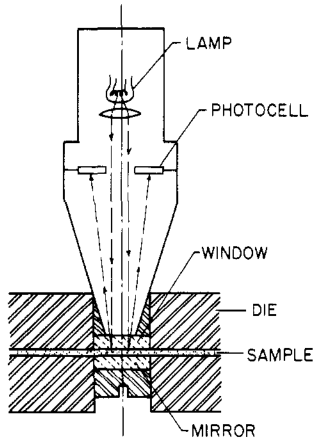

Figure 3. Cross section through die showing optical system.

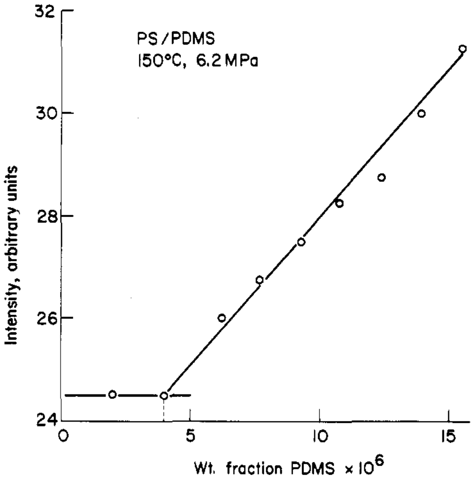

Figure 4. Titration result for the system polystyrene/poly(dimethylsiloxane).

The arrangement of the detector on the die is shown in Figure 3. The detector (Photovolt no. 670) has a conical end which fits in the metal insert and rests directly on the surface of the glass window. The collimated light beam is aligned perpendicular to the glass mirror; any light scattered at a low angle by the sample enters the photocell in the detector, while the unscattered reflected beam is passed back to the light source.

Initially, about 225 g of the polymer is circulated in the system and forms a clear film in the die. Since the film is clear, no light from the detector is scattered and there is no change in the scattering intensity. After a steady base line (constant intensity) is obtained, the second polymer is added from the syringe pump at a very low flow rate (0.1–0.2 mL/min). The concentration of the polymer in the solvent is adjusted to allow several residence times to pass before the cloud point is reached. The high temperature in the hopper and feed section of the extruder forces evaporation of the solvent from the blend, leaving the second polymer (plus a small amount of antioxidant). Because of the high shear in the extruder there is thorough mixing of the two components. Also, high pressure in the system keeps the film free of bubbles. The film remains clear while there is only one phase in the extruder and starts becoming cloudy as the second phase forms. At low amounts of the second phase, the intensity of scattered light increases in direct proportion to the concentration of the second component. The cloud point is, thus, located from the intersection of the base line and the linearly increasing portion of the intensity response. Solubility of the second polymer in the first polymer is then calculated from the flow rate and concentration in solution of the second component.

Results

The results for the system polystyrene (PS)/poly(dimethylsiloxane) (PDMS) are shown in Figure 4. The solubility of PDMS (M_w = 71 800) in PS (M_w = 500 000) is 4×10^{-6} g of PDMS/g of PS. The range of repeat runs is typically 10% of the mean. Clearly, this demonstrates the usefulness of this technique to measure the very low miscibilities typically found in polymer blends; however, with the currently used detection technique, only polymers with different refractive indices can be used.

Although a major portion of the solvent is removed from the blend near the hopper, there is a small quantity left. To minimize any solvent effect, we intend to use a two-stage screw with ring restriction in the extruder and apply vacuum at a vent to devolatilize the blend completely.

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Dilute-Solution Parameters for a Fluorene-Containing "Cardo" Polyquinoline

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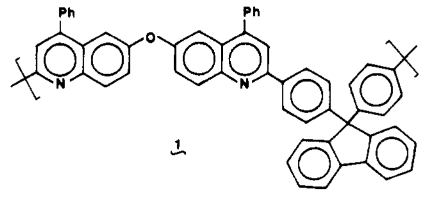
Polyquinolines with totally aromatic bulky cyclic groups serving as loops along the main chain have been prepared.[1] These "cardo" polyquinolines, which are highly amorphous, exhibit high glass transition temperatures (300–420 °C), excellent thermal stability (T_d > 500 °C in air, TGA), and good solubility. Because of this excellent solubility, "cardo" polyquinoline 1, derived from 9,9′-bis(4-acetylphenyl)fluorene and 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, was chosen to study the effect of incorporating a cardo fluorene group on the dilute-solution properties. Polyquinoline 1 is soluble in chloroform, in *sym*-tetrachloroethane (TCE), and in the polymerization medium consisting of di-*m*-cresyl phosphate and *m*-cresol.[2]



1

Experimental Section

Polymer Synthesis. Polyquinoline 1 was synthesized by the acid-catalyzed Friedlander polycondensation of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with 9,9′-bis(4-acetylphenyl)fluorene in a polymerization medium consisting of di-*m*-cresyl phosphate and *m*-cresol at 135–140 °C for a period of 48 h according to the general procedure.[1,2]

Table I
Molecular Weight and Viscosity Data for Fractionated Samples of Polymer 1

fraction no.	$[\eta]_{TCE}$, dL/g	$\bar{M}_n \times 10^{-5}$	$A_2 \times 10^3$, (cm^3·mol)/g^2
1	3.34	5.25	1.36
2	2.63	3.14	1.38
3	1.97	1.59	1.36
4	1.25	1.07	1.38

Intrinsic Viscosity. Solution viscosity measurements on polymer solutions were carried out in Cannon-Ubbelohde microdilution viscometers No. 50 (chloroform) and No. 75 (TCE) at 25.0 ± 0.2 °C. The intrinsic viscosity was obtained from extrapolation of the plots of η_{inh} and η_{red} vs. concentration to zero concentration.

Molecular Weight Determination. A Hewlett-Packard high-speed membrane osmometer (HP-501) equipped with a Schleicher and Schull membrane (S&S Type 08) conditioned in TCE was used to determine $\bar{M}_n$ on fractionated samples. To a stirring solution of 9.1 g of the polymer in 910 mL of chloroform at room temperature was added slowly the nonsolvent ethanol, until the appearance of a slight turbidity. This solution was allowed to stand at room temperature overnight. The clear solution was decanted from the gel phase and the process repeated several times. The gel was dried, redissolved in chloroform, and precipitated into ethanol containing a small amount of triethylamine. The fibrous polymer was suspended in a small amount of ethanol containing triethylamine and chopped in a blender. The polymer was collected by filtration, air-dried, and dried further at 110 °C (0.1 mm) for 24 h. Thus, four fractions were obtained. Intrinsic viscosity and number-average molecular weight for each of the fractions in TCE were obtained at 25.0 ± 0.2 °C and the results are shown in Table I.

Results and Discussion

The dependence of the osmotic pressure (π) on concentration (C) was found to be linear. Therefore, the data were analyzed according to the equation[3]

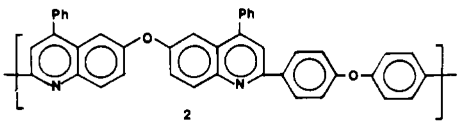
$$\pi/C = RT(1/\bar{M}_n + A_2C) \qquad (1)$$

The intercept obtained by a plot of π/C vs. C was used to calculate $\bar{M}_n$ (Table I). From the number-average molecular weights and the intrinsic viscosities of the various fractions (Table I) it was possible to calculate the constants in the Mark–Houwink equation:

$$[\eta] = KM^a \qquad (2)$$

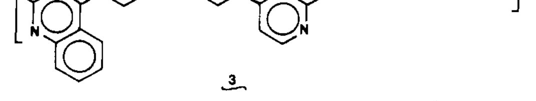
Thus, for 1 in TCE at 25 °C, $K = 1.63 \times 10^{-3}$ and $a = 0.58$. This exponent a, in conjunction with the A_2 value of 1.3×10^{-3} (cm^3·mol)/g^2, indicated good polymer–solvent interaction.

The Mark–Houwink parameters that have been reported[4,5] for other polyquinolines are



2

$[\eta]_{CHCl_3} = 9.0 \times 10^{-4}\ Mn^{0.66}$ $\quad A_2 = 2.96 \times 10^{-3}$ cc-mol/gram^2



3

$[\eta]_{CHCl_3} = 5.5 \times 10^{-3}\ Mn^{0.44}$ $\quad A_2 = 1.48 \times 10^{-3}$ cc-mol/gram^2

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