

Detection of Modifiers in Natural Materials by Catalyzed Polymerization of Styrene

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INTRODUCTION

In a previous communication¹ the effects of several inhibitors and retarders at varying concentrations on the catalyzed polymerization of styrene were reported. Plots of extent of polymerization versus time for the various modifiers were found to be of three different types. Data obtained with these regulators at varying concentrations were used to show relationships of regulator concentration to polymerization rates, inhibition times, and intersection points. As a result of these correlations, the possibility was suggested of using this experimental technique to detect the presence, in complex natural materials of those types of substances which are capable of modifying the catalyzed polymerization of styrene. The presence of free radicals, in particular, might be detected, since electron-spin resonance measurements have shown that natural materials, including petroleum crudes² and coals,³ contain free radicals.

EXPERIMENTAL

The dilatometer, dilatometric measurement measurement methods, and polymerization techniques used in this investigation are the same as those described previously.¹

Viscosity Determinations

The reaction mixture taken from the dilatometer or from sealed test tubes was kept in a refrigerator at -18°C . until viscosity measurements were made. One milliliter of the cold mixture was pipetted into a measured 10-ml. volume of benzene. The viscosity of the resulting solution was determined by measuring its flow time at 25°C . in an Ostwald capillary-type viscometer. Polymerization occurring during the viscosity measurement was assumed to be negligible. Relative viscosities were determined with the use of benzene as the reference liquid.

Materials

Nickel protoporphyrin IX was obtained by the usual method⁴ from protoporphyrin IX derived from hemoglobin.⁵

Wilmington crude oil from Wilmington, California, was stored before use under a nitrogen atmosphere.

Eureka gilsonite and fractions derived therefrom were supplied by the American Gilsonite Company. Pulverized gilsonite (1 kg.) from the Eureka vein was extracted with 5 l. of hexane at 37°C . for 2-3 hr. The insoluble portion was removed by filtration, washed with hexane, and air-dried to give the asphaltene fraction (60%). The solvent was evaporated from the filtrate by heating to 205°C . at 50 mm. pressure, leaving a solid, the resin fraction, in an amount of 40%. The giltenes were obtained from the resin fraction by a chromatographic procedure described previously⁶ in the amount of 6-7% of the whole gilsonite or 15-18% of the resin fraction.

RESULTS AND DISCUSSION

Gilsonite is a solid bitumen containing approximately 85% carbon, 10% hydrogen, 2.5% nitrogen, and much smaller amounts of sulfur, oxygen, and metals.⁷ Porphyrins are present in gilsonite as nickel complexes.⁸ The similarity of gilsonite to petroleum with respect to the types of compounds present suggested the probable presence of free radicals. This was confirmed by electron-spin resonance measurements, which demonstrated that the asphaltene fraction contained more free radicals than the resin fraction which, in turn, contained more than the giltenes. Thus gilsonite and fractions derived therefrom would be expected to alter the rate of catalyzed polymerization of styrene.

The rate of polymerization of bulk styrene at 86°C . catalyzed by benzoyl peroxide at an initial concentration of $1.79 \times 10^{-3}M$ was determined by

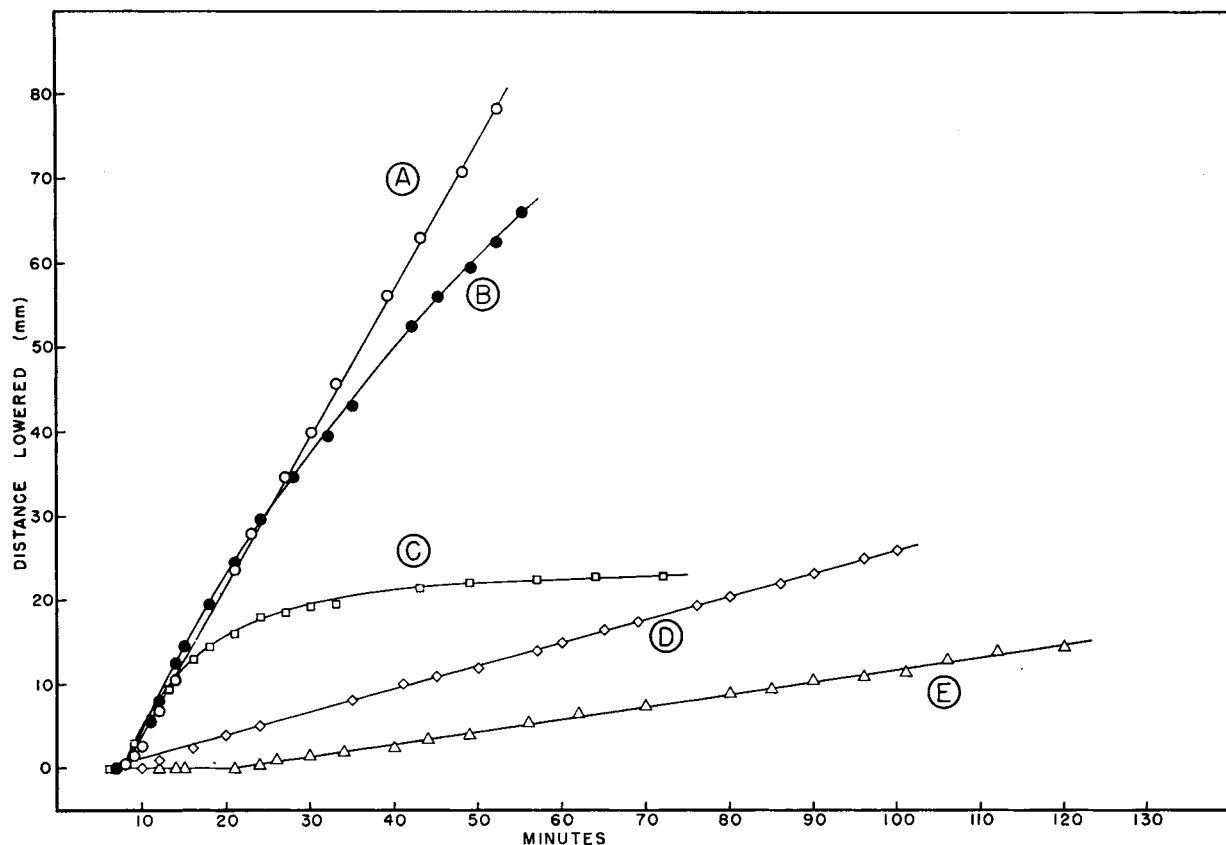


Fig. 1. Dilatometric observation of the bulk polymerization of styrene at 86.6°C. catalyzed by BPO (initial concn. $1.79 \times 10^{-3} M$) in a control run without additive (A) and in runs with the asphaltene fraction of gilsonite as additive at concentrations of 0.67×10^{-3} g./ml. (B); 1.34×10^{-3} g./ml. (C); 2.02×10^{-3} g./ml. (D); 6.72×10^{-3} g./ml. (E).

a dilatometric method.¹ The effects of adding various amounts of certain natural materials to this system were ascertained in much the same fashion as for the synthetic modifiers previously described. Each of the three fractions derived from gilsonite was studied independently. The asphaltene fraction represents the hexane-insoluble portion and the resin fraction the soluble portion of the mineral. The giltenes or oil fraction, derived by adsorption chromatography,⁶ contains the lowest molecular weight and more nonpolar compounds.

Representative data obtained with the asphaltene fraction as the additive are given in Figure 1 and Table I. With increase in the concentration of this fraction, an increase in the inhibition time was observed. The figures obtained are somewhat erratic and subject to error because of the problem of determining zero time¹ and of establishing the time at which polymerization begins, since larger concentrations result in a decidedly retarded rate

subsequent to the inhibition (Fig. 1, curve E). An unforeseen complication attending the runs at lower concentrations was gel formation. In this

TABLE I
Styrene Polymerization with Addition of Gilsonite Asphaltene

Run no.	Asphaltene concn. $\times 10^3$, g./ml.	Inhibition time, min.	Polymerization rate, %/hr.	Reaction time, min.	η_{rel}
178	0.67	0	— ^a	55	— ^a
182	1.34	0	— ^a	72	— ^a
181	2.02	2.5	0.215	100	1.4290
185	2.69	4	0.212	100	1.3347
179	3.36	10	0.185	—	—
184	4.03	9.5	0.171	100	1.1918
188	4.72	9.5	0.146	120	1.1584
189	6.06	10.5	0.109	—	—
183	6.72	14	0.115	120	1.1056
191	7.41	11.5	0.098	—	—

^a Gel formation.

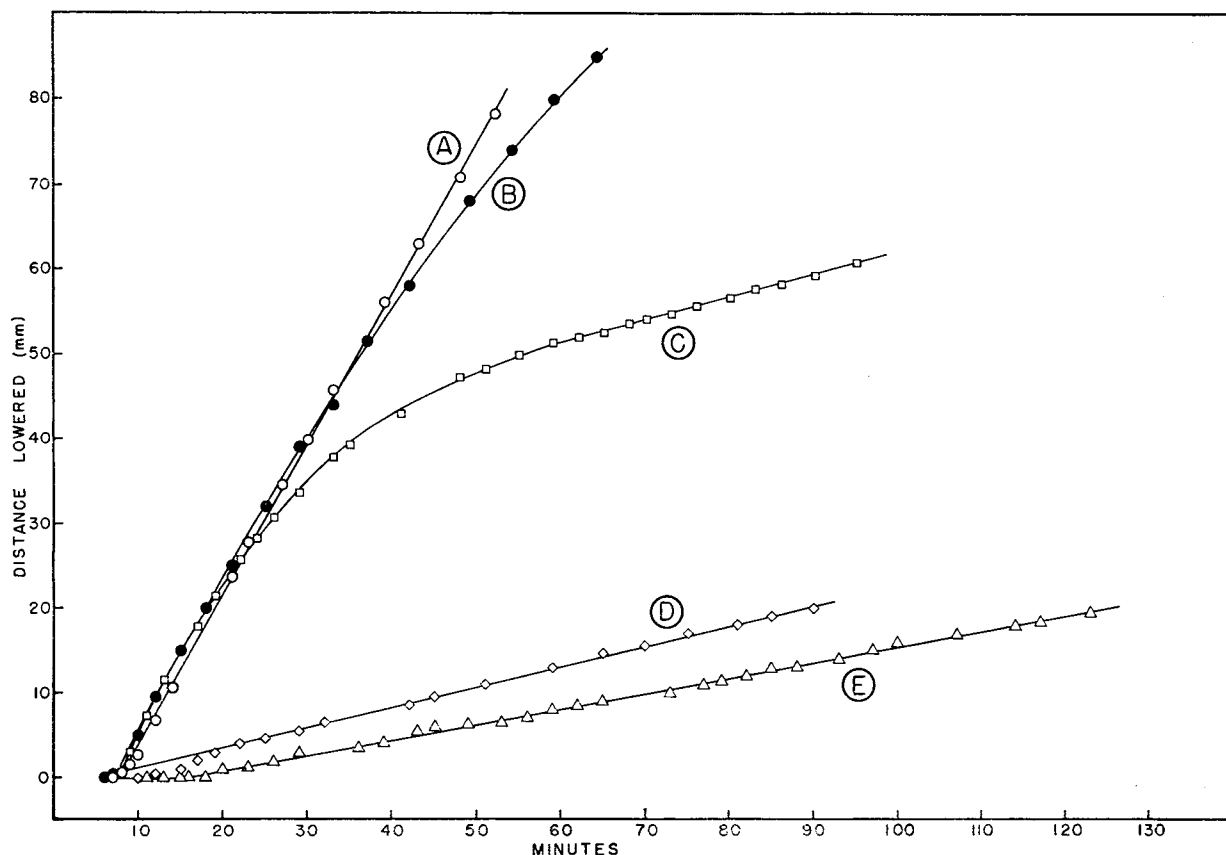


Fig. 2. Dilatometric observation of the bulk polymerization of styrene at 86.6°C. with BPO as catalyst (initial concn. $1.79 \times 10^{-3}M$) in a control run without additive (A) and in runs with the resin fraction of gilsonite as additive at concentrations of 0.71×10^{-3} g./ml. (B); 1.43×10^{-3} g./ml. (C); 4.35×10^{-3} g./ml. (D); 7.28×10^{-3} g./ml. (E).

event, the data derived were not satisfactory for determination of the rate of polymerization (Fig. 1, curve C). Viscosity measurements on the reaction system (Table I) verified the visual observation that higher concentrations of the asphaltene fraction resulted in less viscous media after a given time of reaction. Another change in polymerization

TABLE II
Styrene Polymerization with Addition of Gilsonite Resin Fraction

Run no.	Gilsonite resin concn. $\times 10^3$, g./ml.	Inhibition time, min.	Polymerization rate, %/hr.
172	1.02	0	0.484
167	1.43	0	0.210
174	2.18	0	0.207
169	2.91	0	0.182
176	4.35	3	0.186
177	5.82	6.5	0.149
171	7.28	8.5	0.142

rate occurring at a low concentration of the asphaltene fraction in the system (run no. 178), was an initial acceleration as compared to the control without additive (Fig. 1, curve B). At lower concentrations and inhibition with larger amounts of additive, following an initial acceleration retarded rates of polymerization were observed. (These rates were in every case determined by subjecting the experimental data to a least squares analysis.)

The addition of the resin fraction to the polymerization system provided data (Table II and Fig. 2) similar to that obtained with the hexane-insoluble fraction. As expected, inhibition occurred only at higher concentrations of additive as compared to the asphaltene fraction, as a consequence of lower free radical content. No gel formation or marked changes in viscosity of the polymerization mixture were observed. Acceleration, however, was noted at low concentrations (Fig. 2, curves B and C).

The gilsonite fraction received but cursory attention since addition of widely varying amounts

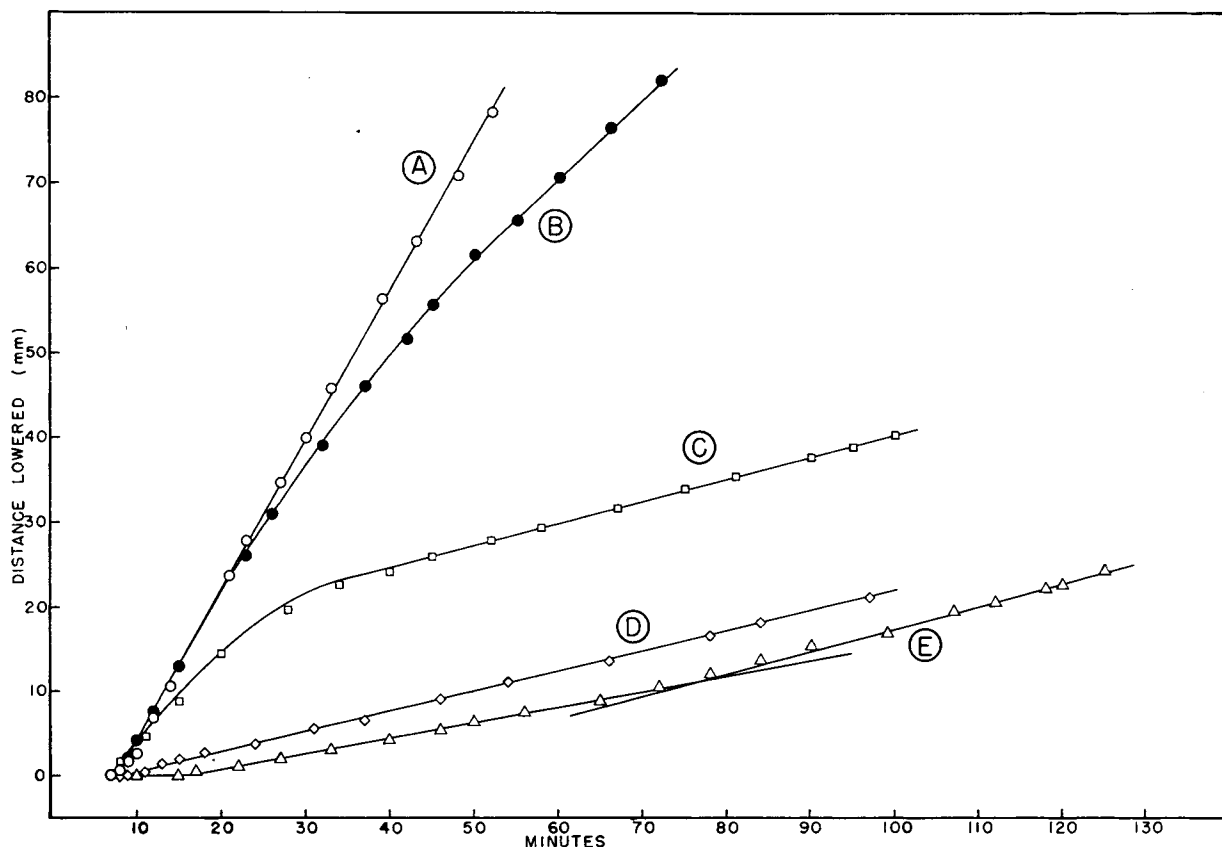


Fig. 3. Dilatometric observation of the bulk polymerization of styrene at 86.6°C. catalyzed by BPO (initial concn. $1.79 \times 10^{-3}M$) in a control run without additive (A) and in runs with Wilmington crude oil as additive at concentrations of 2.05×10^{-3} g./ml. (B); 4.89×10^{-3} g./ml. (C); 8.97×10^{-3} g./ml. (D); 11.42×10^{-3} g./ml. (E).

gave a polymerization rate identical with that of the control system. Apparently the sensitivity of the approach was not sufficient for detection of very low concentrations of free radicals.

The use of whole gilsonite as the additive provided data (Table III) such as would be expected to result from a summation of the effects of each of the fractions. Inhibition times for a given concentration were, in general, intermediate between those for the asphaltene and resin fractions. Gel formation occurred at low concentrations, with viscosities of the reaction mixtures changing in the manner described for the asphaltene fraction. Acceleration of polymerization was observed at low concentrations.

Since gilsonite has been shown⁸ to contain porphyrins as nickel complexes, a study of the effect of a typical metal porphyrin on the rate of polymerization of styrene appeared desirable. Nickel protoporphyrin IX was selected because of its availability. At concentrations of this additive

varying between 0.155×10^{-3} and $1.55 \times 10^{-3}M$, the initial polymerization rates observed were essentially that of the control system with no apparent inhibition, retardation, or acceleration. With larger amounts of additive gel formed, undoubtedly as a result of copolymerization of the

TABLE III
Styrene Polymerization with Addition of Whole Gilsonite

Run no.	Whole Gilsonite concn. $\times 10^3$, g./ml.	Inhibition time, min.	Polymerization rate, %/hr.	Reaction time, min.	η_{rel}
196	0.75	0	— ^a	90	2.323
199	2.26	0	0.224	100	1.407
197	3.76	8.5	0.187	110	1.210
200	5.26	9.5	0.158	110	1.142
201	6.77	7.5	0.119	110	1.098
202	8.27	10.5	0.105	—	—

^a Gel formation.

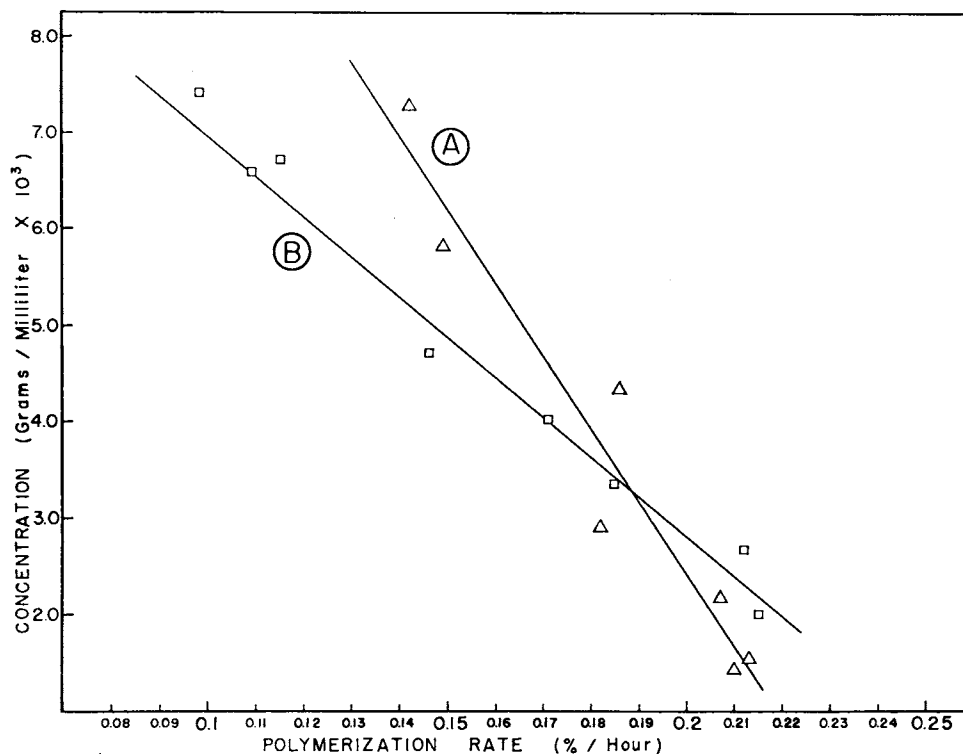


Fig. 4. Final polymerization rate vs. initial concentration of (A) gilsonite resin fraction, (B) gilsonite asphaltene fraction.

porphyrin molecule with the styrene at the site of the vinyl side chain.

Another natural material was studied in much the same manner as gilsonite. Since a great deal of chemical information is available on a crude oil from the Wilmington, California, fields,⁹ the inclusion of this oil in the study appeared desirable. Its effects on the polymerization of styrene were found to follow patterns very similar to those observed with gilsonite. Data are given in Table IV and Figure 3. In general, larger amounts of oil were required to produce a given effect than in the case of whole gilsonite or its asphaltene or resin fractions. Acceleration of polymerization at low concentrations of additive was detectable (Fig. 3, curve B). Gel formation was not observed over the relatively wide range of concentration of additive. With large amounts of additive, inhibition was observed, followed by retarded polymerization (Fig. 3, curve E). Close analysis of the data obtained during the latter period revealed two distinct slopes, the second being the larger. Two different mechanisms of retardation appear to be involved, as was observed also with *p*-benzoquinone and diphenylpicrylhydrazine.¹

The data obtained in the several runs in which natural materials were added to the system were analyzed to determine whether any relationships existed between additive concentration and the polymerization parameters. The retarded but constant rates of polymerization following initial inhibition or acceleration were calculated from dilatometric measurements made for runs with

TABLE IV
Styrene Polymerization with Addition of Wilmington Crude Oil

Run no.	Crude oil concn. $\times 10^3$, g./ml.	Inhibition time, min.	Polymerization rate, %/hr.	
			Initial	Final
209	4.08	0	0.211	0.211
216	4.89	0	0.200	0.200
212	6.52	0.5	0.200	0.200
210	8.15	0.5	0.184	0.184
215	8.97	3.5	0.185	0.185
206	10.23	5	0.157	—
213	10.60	13	0.154	0.190
214	11.42	10	0.143	0.197
211	12.23	11.5	0.149	0.199

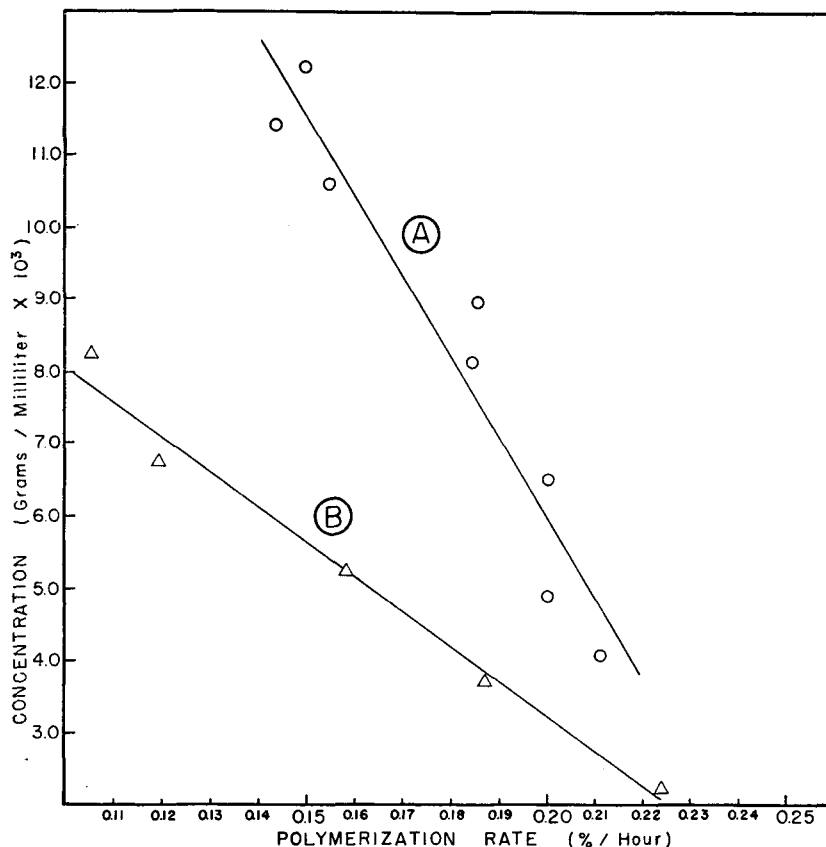


Fig. 5. Final polymerization rate vs. initial concentration of (A) Wilmington crude oil, (B) whole Eureka gilsonite.

various initial concentrations of the several additives (Tables I-IV; Figs. 1-3). These rates were then correlated with initial concentration of additive. The plots of polymerization rates versus initial concentrations of the resin fraction (Fig. 4, line A), the asphaltene fraction (Fig. 4, line B), whole gilsonite (Fig. 5, line B), and Wilmington crude (Fig. 5, line A; the first slope in Fig. 3, line E was used) that show linear relationships. The scattering of points is somewhat greater than that found for similar plots with synthetic modifiers.¹ The effectiveness of the materials in retarding polymerization decreases in the order asphaltene fraction > whole gilsonite > resin fraction > Wilmington crude.

Modifications of the rate of the BPO-catalyzed polymerization of styrene by these natural materials at varying concentrations consist of inhibition, acceleration, and retardation. The question is, whether these different types of reactions involve the same or different molecular species. Since inhibition and retardation are exhibited in the same reaction system with the amount of additive being

the sole variant, a single type of molecular species may be responsible for both effects. A free radical may either initiate or inhibit the polymerization of styrene, depending upon the balance between the rate of addition of radicals to monomer, the rate of interaction of radicals, and the rate of growth of the polymer radicals.¹⁰ A change in the concentration of radicals in the system would alter the extents of these processes. At higher concentrations the interaction of radicals might be the prevailing reaction, leading to inhibition. At low radical concentrations the initiation reaction could prevail. Accordingly, the presence of free radicals with moderate stability in these natural materials could bring about both inhibition and acceleration of styrene polymerization. Even in those runs in which definite inhibition was observed, the data indicate strongly that, during the subsequent initial phase of the retarded polymerization, there was a very brief period of acceleration over the subsequent constant rate (curves D and E of Fig. 2 illustrate this point).

After the additive free radicals were consumed,

a retardation of polymerization occurred. This may have resulted from the variation in types of molecular species present. One additional type of reaction, observed when the asphaltene fraction or whole gilsonite was used as the additive, led to gel formation with increase in the viscosity of the system. It is likely that the crosslinking of linear chains was involved. Since lower concentrations of the additives promoted this effect, it appears that the presence of retarder molecules in the system inhibits this process, and only when the concentration of such a species is decreased does crosslinking occur to an appreciable extent.

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Synopsis

It was determined by dilatometry that the addition of certain natural materials, i.e., gilsonite, the asphaltene and resin fractions derived therefrom, the Wilmington crude oil, to a bulk styrene polymerization at 86.6° C. catalyzed by benzoyl peroxide modified the rate of reaction. At higher concentrations a period of inhibition was observed followed by retarded rates of polymerization. At lower concentrations an initial acceleration occurred, followed by retarded rates of polymerization. The reaction media with smaller amounts of gilsonite or with the asphaltene fraction became appreciably more viscous with time and in extreme cases changed to a gel; under the same conditions the control

system or runs with larger amounts of additives underwent much lesser changes in viscosity. The effect of addition of a metal porphyrin, nickel protoporphyrin IX, was also studied since this type of compound is present in these natural materials. No modification in the polymerization rate was observed. Plots of retarded polymerization rates, observed after initial inhibition or acceleration, versus initial concentration of the several natural additives provided straight lines similar to the relationship found previously for certain synthetic additives. It is proposed that inhibition and acceleration involve natural free radicals in the additives. Gel formation is assumed to result from crosslinking of the polystyrene chains occurring only when natural free radicals and those modifier molecules responsible for retardation are largely spent.

Résumé

On a trouvé que l'addition de certaines substances naturelles: l'ilsonite, l'asphaltène et des fractions de résines dérivant de cette dernière, l'huile brute Wilmington, à la réaction de polymérisation en bloc du styrène à 86,6°C, catalysée par le peroxyde de benzoyle modifie la vitesse de réaction (ceci a été déterminé par dilatométrie). A concentrations élevées, on observe une période d'inhibition, suivie par des vitesses de polymérisation retardées. A basses concentrations, une accélération initiale est suivie par des vitesses de polymérisation retardées. Le milieu de réaction additionné de faibles quantités d'ilsonite ou de fraction d'asphaltène devient nettement plus visqueux en fonction de temps et dans des cas extrêmes se transforme en un gel. Dans les mêmes conditions la viscosité du système de contrôle ou des essais en présence de plus grandes quantités d'additifs sont modifiés dans une moins grande mesure. L'effet d'addition d'une porphyrine métallique, la protoporphyrine IX de nickel, a aussi été étudié puisque ce type de composé est présent dans ces substances naturelles. Aucune modification dans la vitesse de polymérisation n'a été observée. Les diagrammes des vitesses de polymérisation retardée observées après inhibition initiale ou accélération, et de la concentration initiale des nombreux additifs naturels fournissent des droites semblables à celles données par la relation trouvée pour certains additifs synthétiques. Il a été proposé que l'inhibition et l'accélération étaient dues aux radicaux libres naturels inclus dans les additifs. La formation d'un gel est une conséquence du pontage des chaînes de polystyrène avec ce type de réactions qui se produisent seulement lorsque les radicaux libres et les molécules de modificateurs responsables du retardement sont largement consommés.

Zusammenfassung

Der Zusatz von bestimmten Naturstoffen, wie Gilsonit, den daraus erhaltenen Asphalt- und Harzfraktionen und Wilmington-Rohöl, zu einer durch Benzoylperoxyd katalysierten Polymerisation von Styrol in Substanz bei 86,6°C änderte die Reaktionsgeschwindigkeit (mit Hilfe einer dilatometrischen Methode bestimmt). Bei höherer Konzentration wurde eine Inhibierungsperiode mit darauffolgenden, herabgesetzten Polymerisationsgeschwindigkeiten beobachtet. Bei kleinerer Konzentration trat eine anfängliche Beschleunigung und später herabgesetzte

Polymerisationsgeschwindigkeit auf. Die Reaktionsmedien mit geringerem Gehalt an Gilsonit oder Asphaltfraktionen wurden im Laufe der Zeit bedeutend viskoser und wandelten sich in extremen Fällen zu einem Gel; unter den gleichen Bedingungen änderte sich die Viskosität eines Vergleichsversuches oder eines Versuches mit grösserem Additivzusätzen weitaus weniger. Weiters wurde der Einfluss des Zusatzes eines Metallporphyrins, nämlich Nickelprotoporphyrin IX, untersucht, weil dieser Verbindungstyp in den Naturstoffen ebenfalls vorhanden ist. Es wurde keine Änderung der Polymerisationsgeschwindigkeit beobachtet. Trägt man die herabgesetzten Polymerisationsgeschwindigkeiten, die man nach anfänglicher In-

hibierung oder Beschleunigung beobachtet, gegen die Anfangskonzentration der einzelnen natürlichen Additivs auf, so erhält man eine Gerade ähnlich wie man sie bereits früher für bestimmte synthetische Additivs erhalten hat. Es wird angenommen, dass Inhibierung und Beschleunigung durch natürliche freie Radikale in den Additivs verursacht werden. Die Gelbildung wird auf eine Vernetzung der Styrolketten zurückgeführt; dieser Reaktionstyp verläuft aber nur, wenn natürliche freie Radikale und die für die Verzögerung verantwortlichen Moleküle des Zusatzstoffes in grossem Ausmass vorhanden sind.

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