The Effect of Active Carbon on the Kinetics of Polymerization of Methyl Methacrylate

William J. Snyder[a]; Deepak Kunzru[ab]

[a] Chemical Engineering Department, Bucknell University Lewisburg, Pennsylvania [b] University of Pittsburgh, Pittsburgh, Pennsylvania

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The Effect of Active Carbon on the Kinetics of Polymerization of Methyl Methacrylate

WILLIAM J. SNYDER and DEEPAK KUNZRU*

Chemical Engineering Department
Bucknell University
Lewisburg, Pennsylvania 17837

SUMMARY

Rates of 2-2'-azobisisobutyronitrile initiated polymerization of methyl methacrylate in benzene were determined at 77.2, 65.0, and 50.0°C. The variation of molecular weight of the polymer with temperature and conversion was also studied. At a fixed conversion of 2.0%, the molecular weight decreased from 2.05×10^5 at 50°C to 1.4×10^5 at 77.2°C. The ratio of the propagation rate coefficient to the square root of the termination rate coefficient was found to be 0.61, 0.397, and 0.374 at 77.2, 65.0, and 50.0°C, respectively, with an uncertainty of ±0.5°C in temperature.

The effect of active carbon on the rates of polymerization at 77.2°C was measured. Rates of polymerization decreased in the presence of active carbon. For example, the initial rate of polymerization decreased from 7.8×10^{-4} mole/(liter min) to 4.6×10^{-4} mole/(liter min) when the carbon concentration was varied from 0 to 9.65 g/liter. The molecular weight of the polymer increased from an average of 1.4×10^5 in the absence of carbon to 1.5×10^5 when carbon was present.

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*Present address: University of Pittsburgh, Pittsburgh, Pennsylvania

INTRODUCTION

The extent to which chemical processes can occur at surfaces and con-
tinue in the surrounding medium by a series of chain steps involving atoms
and radicals is important not only in respect to the mechanism of chain
reactions of combustion but also in the formulation of mechanism in
enzymic and biological processes.

There is only a limited amount of evidence with respect to the initiation
of reaction at solid surfaces acting as catalysts and the propagation of
chains in the surrounding liquid media. Interactions of this type are
pertinent to the problem of elastomer reinforcement by carbon blacks in
that they may shed some light on the mechanism by which polymer mole-
cules become attached to the carbon surface. A more recent development
has been the use of carbon blacks in polyolefins as protection against photo
and thermal oxidation. Carbon black and activated carbon are excellent
black bodies, absorbing radiation both in the UV and IR regions. Accord-
ingly, when dispersed in polyethylene it preferentially absorbs and dissipates
the incident radiation. Because carbon black also appears to be effective
in terminating free radical chains, it provides protection against thermal
degradation.

Although a large number of investigators have studied the kinetics of
polymerization of vinyl monomers, both bulk and solution, few studies of
polymerization of vinyl compounds by catalytic solids have been reported.

The object of this study was to investigate the effect of activated carbon
on the kinetics of polymerization of methyl methacrylate in benzene. The
influence of the activated carbon on the molecular weight of the polymer
formed was also studied. However, the effect on the mechanical properties
of the polymer was not studied in this work.

REVIEW OF LITERATURE

Methyl methacrylate has been extensively polymerized for the last three
decades. The use of azobisnitriles as initiators was first reported by Arnett
[1]. This work indicated that aliphatic azobisnitriles decompose thermally
in solution by a true first-order reaction not influenced by solvent or con-
centration. It was shown that at a fixed temperature the initial rate of
polymerization of methyl methacrylate is proportional to the first power
of the monomer concentration and to the square root of the initiator con-
centration, thus confirming the free radical mechanism. Imoto et al. [2]

presented the time conversion curves of the azobisisobutyronitrile initiated polymerization of methyl methacrylate. It was shown that the curves were straight lines up to a 10% conversion.

The effect of activated carbon on the polymerization of methyl methacrylate has not been studied. Some investigators have reported the influence of activated carbon and carbon blacks on other polymerizable substances. Hummel [3] describes active carbon as a substance catalyzing polymerization.

Breitenbach and Preussler [4] presented the effect of eight different active carbon preparations on styrene polymerization. They found that the carbon decreased the rate of polymerization. The effect on the molecular weight was not determined. The intrinsic viscosities of the polymer formed were either decreased or increased by the addition of active carbon, depending upon the activity of the carbon sample used. They observed that the retarding effect was caused by the added carbon and not by the adsorbed oxygen or any other contaminant. Moreover, the active carbon did not react with the "dead" polymers. Therefore, it was postulated that the viscosity increasing effect, as well as the polymerization rate retarding effect, must be related to some form of reactivity of growing live polymer.

Kraus et al. [5] studied the effect of various carbon blacks on the free-radical thermal polymerization of styrene and "found strong evidence of inhibition caused by surface quinone groups." They reported that the typical rubber reinforcing blacks inhibited polymerization initially but accelerated the rate at the end of the induction period. Monomer decanted from the black polymerized at the normal rate, showing no soluble constituents, but the carbon surface must be the locus of polymerization activity. They did not give any mechanism for the accelerated effect of polymerization.

Medalia et al. [6] carried out a number of solution polymerizations of styrene with azobisisobutyronitrile (AIBN) as initiator in the presence of various carbon blacks. The general, induction periods were obtained, followed by polymerization close to the rate found in the absence of black. They postulated that a number of radicals presumably react with the carbon black, as small polymer chains rather than as primary AIBN radicals, during the induction period. The number of radicals was of the same order of magnitude as the number of quinone groups for furnace blacks, but smaller than the number of quinone groups for the channel blacks. Unlike the theory suggested by Kraus et al., the reaction of radical with the carbon black involves only a portion of the quinone groups.

The effect of carbon black on the solution polymerization of vinyl acetate was also presented by Medalia et al. The induction periods were much shorter than for styrene, but the retardation was more pronounced. No mechanism for this behavior was given.

EXPERIMENTAL APPARATUS AND PROCEDURE

The purpose of the investigation was to study the effect of activated carbon on the solution polymerization of methyl methacrylate in benzene. AIBN was used as initiator.

First, normal polymerization (without active carbon) was carried out at 77.2, 65.0, and 50.0°C. Then, the polymerization was studied at 77.2°C, using three different concentrations of the activated carbon. For each case, the change in molecular weight of the polymer, during the course of the reaction, was measured.

Equipment

Polymerization of methyl methacrylate was performed in an isothermal stirred batch reactor. The stainless steel reactor (Fig. 1) contained baffles, a variable speed stirrer, and cooling coils. The reactor was also equipped with a heating mantle with a capacity of 700 W. The reactor was 5 ¾ in. in diameter, 9½ in deep, and contained 3.65 liters. The reactor was maintained at a constant temperature by a Yellow Spring Temperature Controller (on-off type) with a range from –5 to +125°C and capable of controlling a full reactor to ±0.5°C.

The temperature of the contents of the reactor was determined by a copper Constantan thermocouple (A)* placed in the stainless steel thermocouple well. The thermocouple was also provided with a reference junction kept at 0°C so that the temperatures could be read directly without making room temperature corrections.

The sampling system consisted of a three-way valve (C) such that either nitrogen could be passed through it or samples could be removed. Throughout the experiment, except when samples were taken, the valve was in a position that allowed the nitrogen to flow in the reactor. The nitrogen stream forced back any reaction mixture remaining in the lines after sampling.

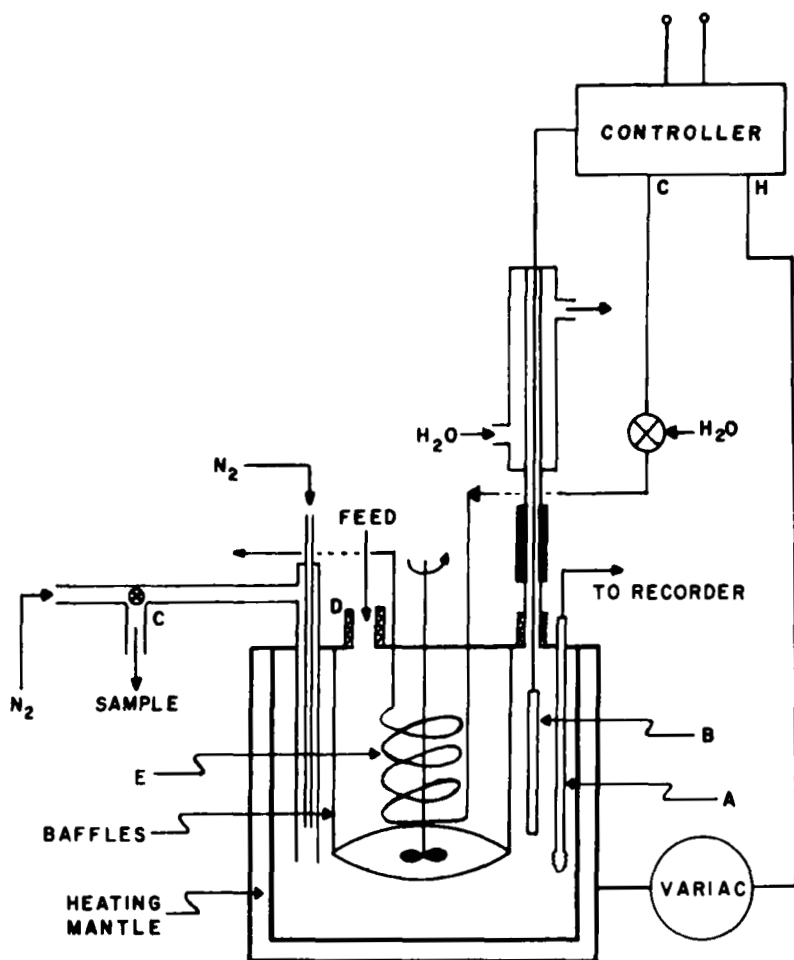*Letters in parentheses refer to Fig. 1.

Fig. 1. Experimental apparatus.

All connections and fittings were of stainless steel. No brass connections were used because it has been established that copper, even if present in trace quantities, can affect the polymerization.

The reactor was provided with a condenser to trap any benzene vapors. The temperature sensor (B) from the controller passed through the condenser into the reaction mixture. The wires of the temperature sensor were taped with Teflon to avoid contamination.

Table 1. Properties of Activated Carbon (Nuchar WV-G 12 × 40)

Specificatons [8]

Iodine number, minimum	1050
Abrasion number, minimum	75
Moisture when packed (%), maximum	2
Ash (%), maximum	8.5
Particle size (U.S. Sieve Series)	12 × 40
Oversize (%), maximum	5
Undersize (%), maximum	5

Typical properties

Apparent density (lb/ft^3)	27.5
Surface area (nitrogen BET method) (m^2/g)	1100
Particle density, wetted in water (g/cc)	1.4
Effective size (mm)	0.65
Uniformity coefficient	1.60
Voids in packed bed (%)	40

Procedure

Methyl methacrylate monomer, pure grade supplied by Eastman Organic Chemicals, was washed with a 5% sodium hydroxide to remove the inhibitor. The inhibitor-free monomer was washed with distilled water and dried with calcium chloride. Benzene (Baker Chemical), certified grade, was charged to the reactor and heated under a nitrogen atmosphere to the desired temperature. The monomer and initiator were added according to the following recipe: 125 g of methyl methacrylate, 0.1 g of AIBN (Eastman Organic Chemicals), and 900 g of benzene.

Samples were taken from the reactor with a graduated syringe at various times and the polymer containing syrup poured into 250-300 ml of methanol (Baker Chemicals, reagent grade). The resulting flocculent polymer was filtered, washed with methanol, and dried.

In experimental runs containing carbon, a carbon-benzene slurry was the initial charge. Properties of the carbon used are listed in Table 1. The previously mentioned procedure was followed except the carbon-containing

polymer was redissolved in benzene and the activated carbon separated from the polymer. Both polymer and carbon were dried and weighed.

The dried polymer was used for determining the average molecular weight. Intrinsic viscosity measurements were made in a Ubbelohde dilution viscometer at $30 \pm 0.05°C$ with thiphene-free benzene as a diluent. Viscosity-average molecular weights were calculated from the relationship

$$[\eta] = K\overline{M}_v{}^a$$

For polymethyl methacrylate in benzene at $30°C$ the values of

$$K = 5.2 \times 10^{-5}$$

$$a = 0.76$$

as determined by Cohn-Ginsberg et al. [7] were used to determine molecular weights.

RESULTS

Reaction rates were measured at three different temperatures in the absence of carbon and then at $77.2°C$ for three different carbon concentrations.

Rate of Polymerization at Different Temperatures in the Absence of Carbon

Polymerization of methyl methacrylate was carried out at 77.2, 65, and $50°C$. The two initial samples were taken at 15 min intervals and the remaining samples were taken every 30 min over a period of 3 hr. The initiator and monomer concentrations were 5.9×10^{-4} and 1.205 moles/liter, respectively, for all runs. The time conversion curves shown in Fig. 2 are linear up to about 12% polymer and show good agreement with results obtained by Arnett [1] and Imoto [2].

The variation of molecular weight with temperature at 2% conversion is shown in Fig. 3. For the same conversion, the lower the temperature, the higher the molecular weight. However, the variation of molecular weights with conversion is small. Using the data from Fig. 2, the initiator efficiency [6] of 0.6, and the expression given by Van Hook and Tobolsky [9] for k_d in sec^{-1} where

$$k_d = 1.58 \times 10^{15} \exp \left(\frac{-30.8}{RT} \text{ kcal} \right)$$

the values of $k_p/k_t^{1/2}$ were obtained at three different temperatures. Table 2 indicates that the ratio of rate coefficients increases with increasing temperature as expected. These values are 40% lower than Arnett's [1] values of 1.09 at 77°C and 0.67 at 50°C. The difference in activation energies, i.e., $E_p - E_t/2$ was found to be 5.32 kcal compared to 4.9 kcal reported by Matheson and 4.0 kcal by Arnett. Because these investigators did not study the variation of molecular weight with temperature, a comparison of results could not be made.
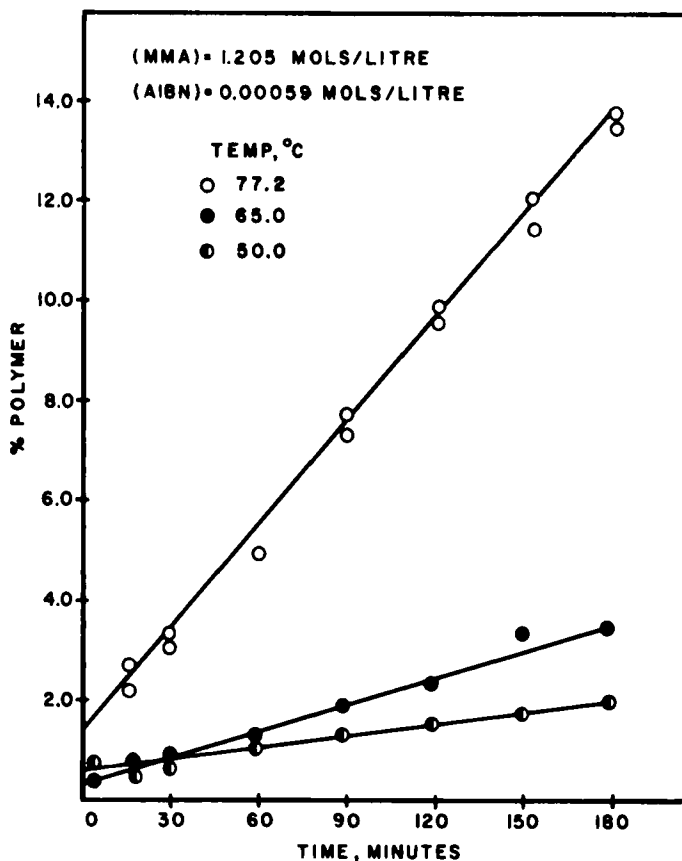
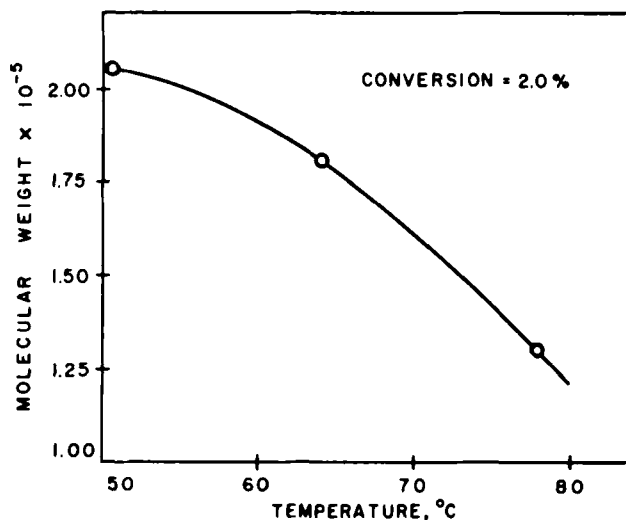**Fig. 2.** Effect of temperature on the rate of polymerization.

Fig. 3. Variation of molecular weight with temperature.

Table 2. Ratio of Rate Coefficients at Various Temperature

Temperature (°C)	$k_p/k_t^{1/2}$ without carbon	$k_p/k_t^{1/2}$ with carbon	g of carbon/lt
77.2	0.660	0.516	0.965
77.2	0.630	0.458	4.875
77.2	0.570	0.308	9.65
77.2	0.590	-	-
65.0	0.394	-	-
65.0	0.399	-	-
50.0	0.379	-	-
50.0	0.369	-	-

Rate of Polymerization in the Presence of Active Carbon

The active carbon used in this study decreased the rate of polymerization and increased the intrinsic viscosity. Therefore, the carbon increased the degree of polymerization, i.e., the carbon promotes longer chains. To gain further insight on this phenomenon, the active carbon was examined for the presence of polymer in the pores. The active carbon in a sample was dried,
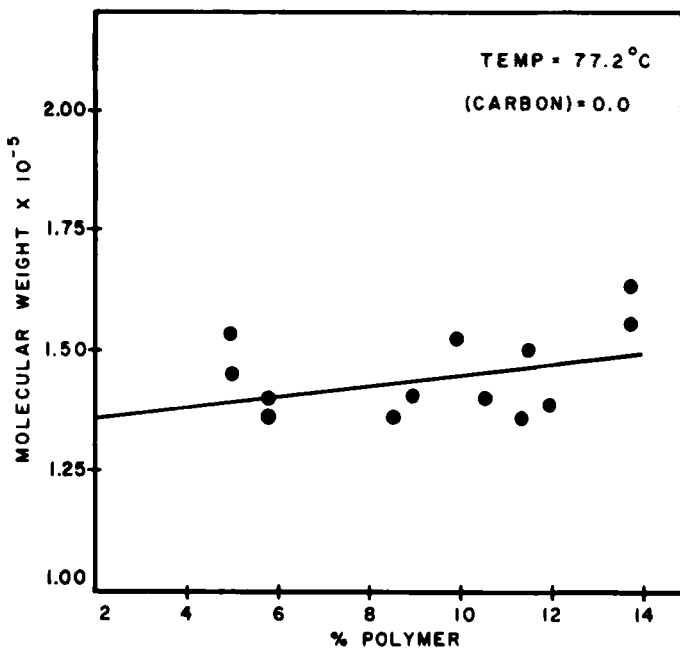
TEMP = 77.2°C

(CARBON) = 0.0

Fig. 4. Variation of molecular weight with conversion.

weighed, and stirred in benzene for 4 hr. The benzene was decanted and the carbon dried. Because no significant decrease in the weight of active carbon could be detected, it was concluded that no polymer formed in the pores of the carbon. However, it is quite possible that benzene would fail to dissolve a very high molecular weight polymer. Further investigation of pore polymerization is needed.

The time conversion curves of the AIBN initiated polymerization of methyl methacrylate with 1, 5, and 10 g of active carbon in 0.9 liters of benzene are shown in Fig. 4. The curves are linear up to a certain conversion which varies with the concentration of carbon. For example, at a carbon concentration of 0.965 g/lt, the curve is linear only to 8% convertion, but at 9.65 g/lt of carbon, the curve is linear only to 4% conversion. The initial polymerization rates are retarded in the presence of active carbon carbon as seen in Fig. 5.

It is seen from Fig. 6 that the molecular weight of the polymer is essentially independent of carbon concentration. However, for the same conversion the molecular weight is higher when activated carbon is present.
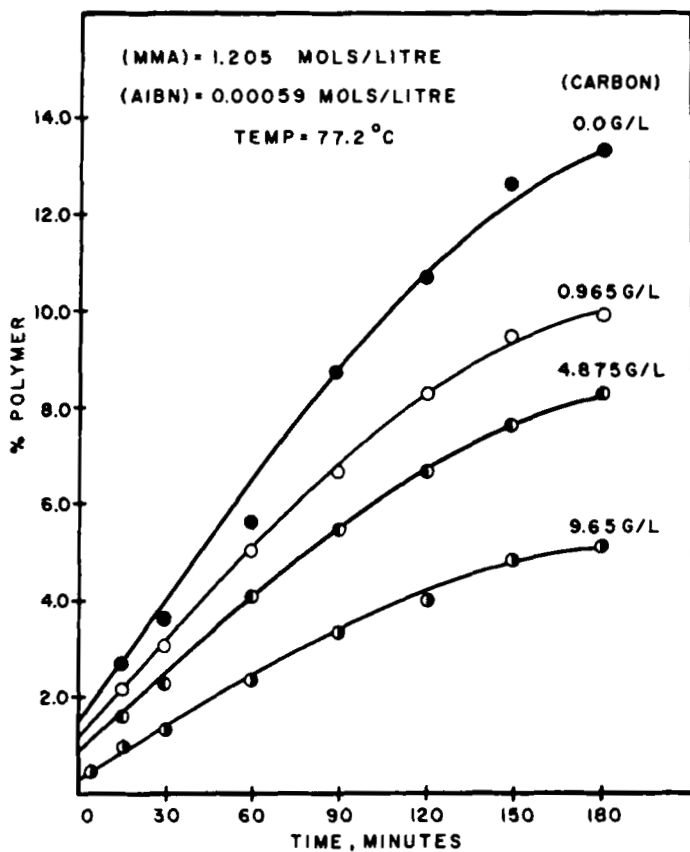
Fig. 5. Effect of Carbon on the rate of polymerization.

The average experimental error in molecular weight determination was ±4200.

CONCLUSIONS

The behavior of the activated carbon in the presence of methyl methacrylate is complex. It retards the rate (Fig. 7) and increases the chain length of the polymer. The possibility that the activated carbon acts as a chain transfer agent can be ruled out because the molecular weight in the presence of activated carbon is greater than the molecular weight obtained without carbon.
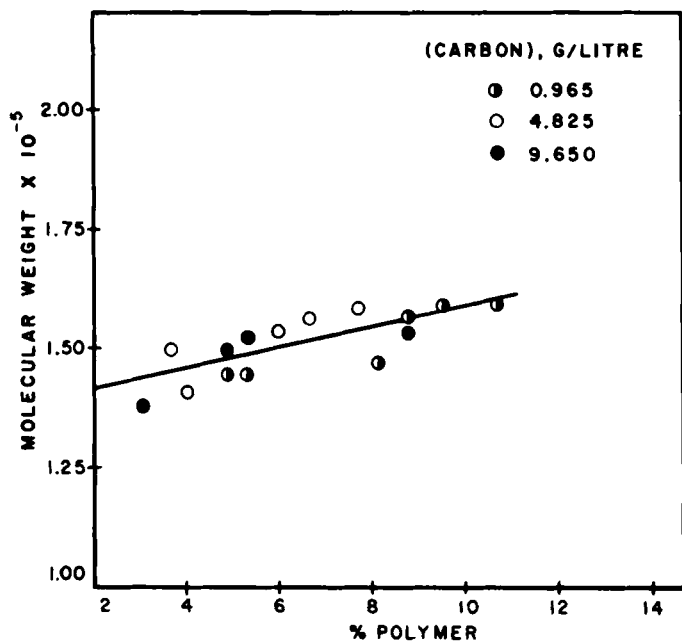
Fig. 6. Variation of molecular weight with conversion in the presence of carbon.
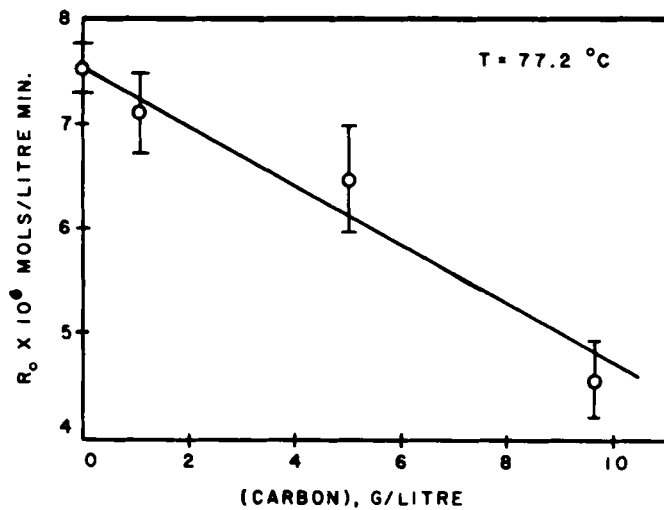

Fig. 7. Initial rate of polymerization at $77.2°C$ as a function of carbon concentration.

The results of this work are consistent with the trends obtained by other workers. As already mentioned earlier, Breitenbach and Preussler [4] reported that "all the carbon preparations examined decreased the rate of polymerization to some extent." In their work, some preparations decreased the molecular weight while others increased the molecular weight. In addition, these workers found that the retarding effect was caused by the added carbon and not by adsorbed oxygen or any other contaminant.

Medalia et al. [6] presented the results for the effect of carbon black on styrene and vinyl acetate polymerization. However, they did not give any reasons to explain this behavior. The results of our work are similar to the results obtained for vinyl acetate polymerization in the presence of carbon black [6]. Our work is in agreement with Madalia's results which indicates that the time converging curves are linear up to a certain extent.

Certain active groups take part in the polymerization, but the nature of exact mechanism is uncertain. With the present data and equipment, it was not possible to identify these groups.

NOMENCLATURE

a: exponent in viscosity equation

E_p, E_t: activation energies of chain propagation and termination

K: constant in viscosity equation

k_p: propagation rate coefficient, liters/mole min

k_t: termination rate coefficient, liters/mole min

$\overline{M}_v$: viscosity-average molecular weight

$[\eta]$: intrinsic viscosity

ACKNOWLEDGMENT

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