Effect of the Concentration of Phenyldichlorophosphine and Reaction Time on the Intrinsic Viscosity of Copolymers of Methyl Methacrylate with Phenyldichlorophosphine

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Synopsis

The relation between the intrinsic viscosity of methyl methacrylate–phenyldichlorophosphine copolymers and the copolymerization time were investigated. The copolymers of methyl methacrylate and phenyldichlorophosphine were prepared at mole ratios of 1:10.012, 1:0.026, and 1:0.062, respectively. The experiments indicate that the intrinsic viscosity of copolymers increases at the first stage of copolymerization and then decreases after reaching a maximum. These changes of the intrinsic viscosity can be explained by degradation and by small relative activity of organophosphorus comonomers.

Introduction

Studies on the extent of copolymerization of methyl methacrylate with phenyldichlorophosphine[1] indicate that concentration of phenyldichlorophosphine in the reaction mixture affects obviously the reaction run. Determinations of the intrinsic viscosity of copolymer samples prepared with various contents of phenyldichlorophosphine were expected to supply more data regarding the reaction. The same determinations were carried out for copolymer samples obtained at various intervals of reaction duration.

Discussion of Experiments

Copolymerization of methyl methacrylate with phenyldichlorophosphine was carried out by a conventional bulk method.[2] In all experiments azobisisobutyronitrile was used as a catalyst. Viscosities were measured on an Ostwald viscometer at 20 ± 0.01°C., a Beckman thermometer being used to follow temperature. For each sample of copolymer two sets of viscosity measurements were carried out; one on copolymer samples containing unreacted monomers and a second for copolymers free from monomers. The monomers were removed from copolymer by dissolution of the sample in chloroform and precipitation with petroleum ether. The precipitated copolymer was washed with petroleum ether on a filtering crucible and dried under reduced pressure at room temperature until the constant weight

had been achieved. The intrinsic viscosities of copolymers of methyl methacrylate (M_1) with phenyldichlorophosphine (M_2) mixed at (M_1/M_2) mole ratios of 1:0.012, 1:0.026, and 1:0.062 and prepared at 60°C. for various periods of reaction time, were measured. The results are plotted in Figures 1 and 2.
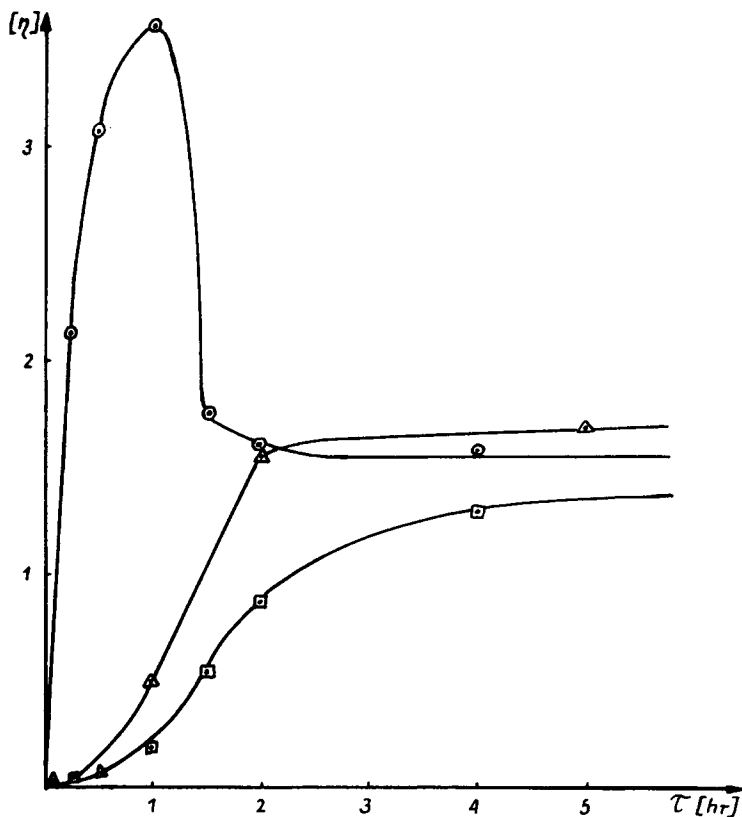

Fig. 1. Relationship between the intrinsic viscosity of copolymer solutions in chloroform and the copolymerization time at various methyl methacrylate (M_1): phenyldichlorophosphine (M_2) mole ratios: (⊙) 1:0.012; (△) 1:0.026; (□) 1:0.062.

To get better knowledge of changes involved during copolymerization of methyl methacrylate with phenyldichlorophosphine, the effect of phosphorus content on the reaction time was investigated for copolymer prepared at M_1/M_2 a mole ratio of 1:0.026. The phosphorus content in copolymer samples was determined by a colorimetric method. The results are summarized in Table I. For the purpose of comparison, the effect of the copolymerization time on phosphorus content, the extent of reaction, and the intrinsic viscosity of copolymer solutions with monomers and free from monomers is plotted in Figure 3.

TABLE I

Effect of the Time of Copolymerization of Methyl Methacrylate (M_1) with
Phenyldichlorophosphine (M_2) on the Content of Phosphorus in the Copolymer

Copolymerization time, hr.	Extent of reaction, %	Phosphorus in copolymer, %
		0.17
0.27	7.36	0.18
0.50	50.17	0.26
		0.28
1.00	76.21	0.54
		0.52
2.00	87.37	0.56
		0.60
5.00	95.84	0.59
		0.56
24.00	98.29	0.60
		0.59

Discussion of Results

In the case of copolymerization of methyl methacrylate with phenyldichlorophosphine, the relation between the intrinsic viscosity of the copolymerized products and the copolymerization time is easily seen.

At the first stage of copolymerization, the viscosity of copolymerized products increases and it reaches a maximum after about 1 hr.; then, a decrease is observed. Such a pattern of changes of the intrinsic viscosity of copolymers makes interpretation of results very difficult. Taking into account changes of phosphorus content in the copolymer, the extent of reaction, and changes in the intrinsic viscosity in relation to the copolymerization time, the following scheme of copolymerization may be suggested.

In the first stage of copolymerization the internal energy of the comonomers–initiator system is very low, and segments of macromolecular chains built mainly of methyl methacrylate homopolymer are formed. Then, a decay of initiator produces a great number of free radicals, and the internal energy of the whole system increases rapidly. Now, the energy level of the system is so high that phenyldichlorophosphine molecules are excited too, and they begin to play an active part in copolymerization.

At the next stage, the internal energy of the system decreases as the result of disappearance of free radicals and the exothermic character of copolymerization. This process is observed at an extent of reaction just over 80%. In this stage a decrease of the intrinsic viscosity of copolymer solutions is noted. Changes of the intrinsic viscosity as characterized by the shape of the curve shape may be interpreted on the one hand as due to the low copolymerizability phenyldichlorophosphine and on the other as attributable to some processes leading to degradation of macromolecules formed.
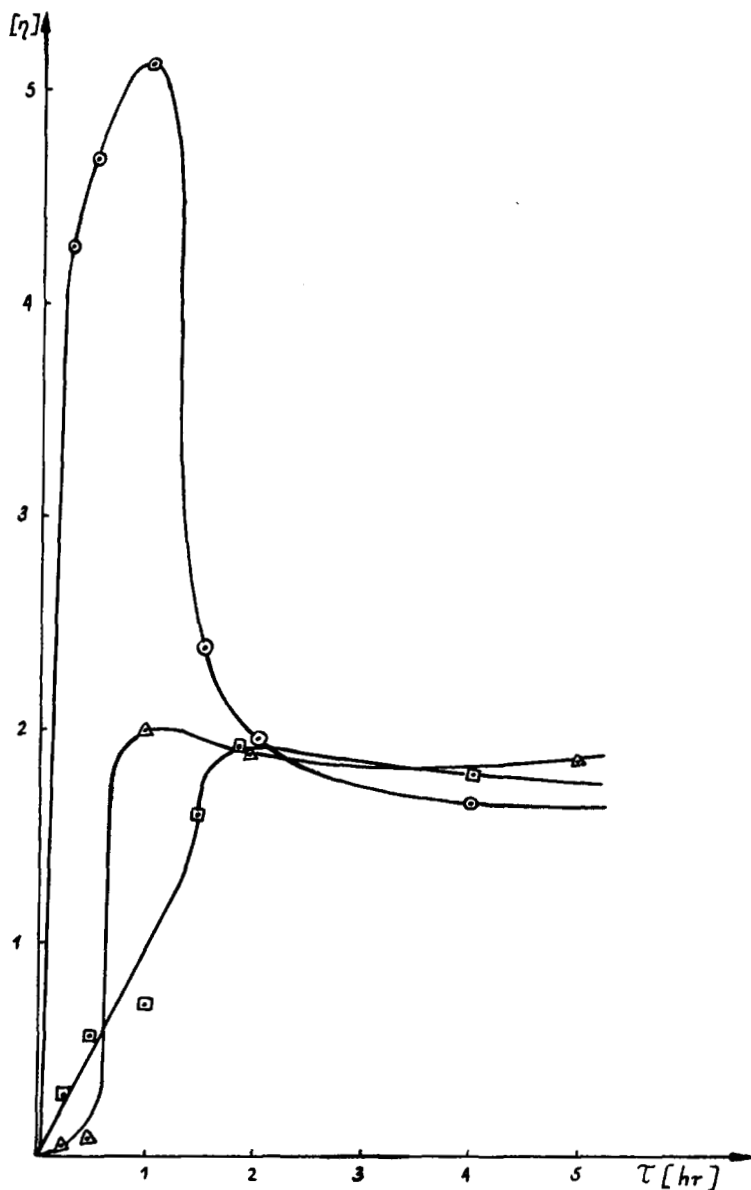
Fig. 2. Relation between the intrinsic viscosity of chloroform solutions of copolymers free from monomers and the copolymerization time at various M_1/M_2 mole ratios: (⊙) 1:0.012; (△) 1:0.026; (⊡) 140.062.

At last stage of copolymerization the ratio of phenyldichlorophosphine to methyl methacrylate monomers is much larger than it was at the beginning; thus free radicals are trapped rapidly by phenyldichlorophosphine, growth of macromolecules is stopped, and only macromolecules of low polymerization degrees are formed.
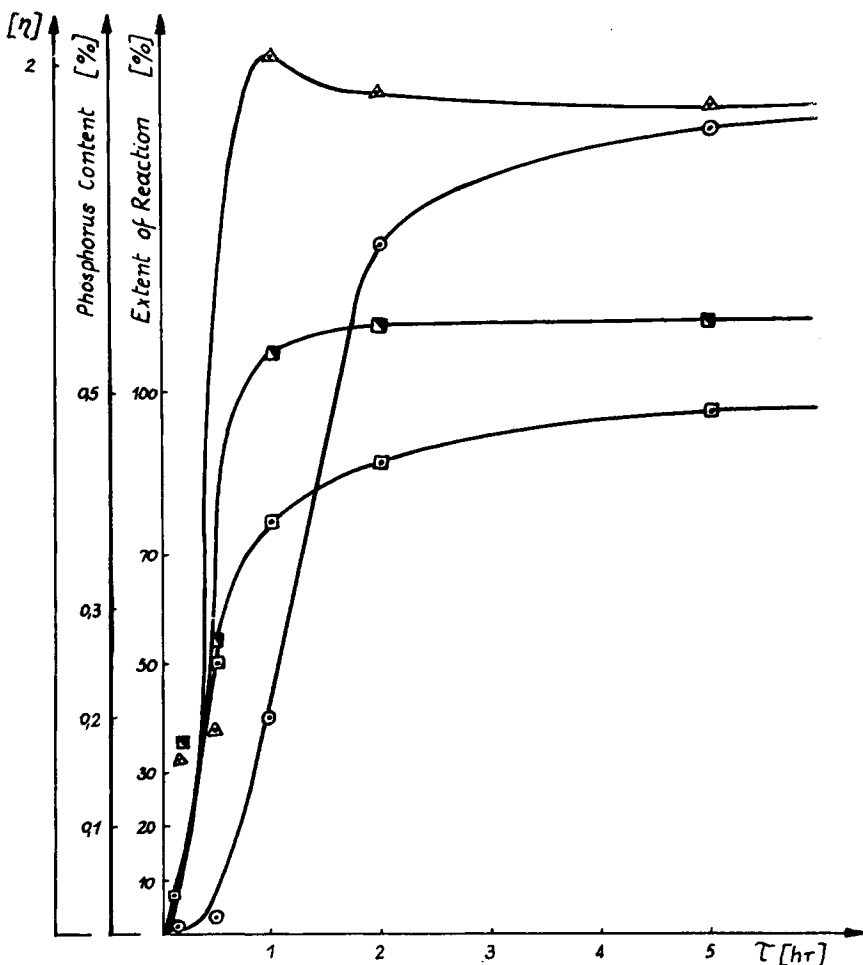
Fig. 3. Influence of the copolymerization time on: (■) phosphorous content of the copolymer; (□) extent of reaction; (○) intrinsic viscosity of chloroform solution of monomer free copolymer; (△) intrinsic viscosity of chloroform solution of copolymer with unreacted monomers.

This scheme is in good agreement with works of Michalski et al.,[3,4] who showed that trivalent phosphorus can act as an electron acceptor in organophosphorus compounds, including phenyldichlorophosphine.

The studies of Barb[5,6] indicate that two non olefinic molecules cannot participate in semi-vinyl copolymerization. Thus, it seems that at the end of the copolymerization process of methyl methacrylate (M_1) with phenyldichlorophosphine M_2 short chain macromolecules are formed, having a chemical formula approximately of the type $M_2M_1M_2M_1M_2M_1M_2$. From this it may be deduced that at the final stage of copolymerization the average molecular weight of copolymer is decreased. This supported results

of intrinsic viscosity determinations on copolymer samples free from mono-mers. A distinct maximum on the intrinsic viscosity curve (Figs. 1 and 2) is seen for monomer-free copolymers, while the intrinsic viscosity of copoly-mer samples containing unreacted monomers increased over the whole copolymerization time (Fig. 2).

On comparing changes of the intrinsic viscosities of copolymers (Fig. 1) polymerized at the M_1/M_2 mole ratios of $1:0.062$ and $1:0.026$ it is apparent that the intrinsic viscosity maximum is higher at a lower content of phenyl-dichlorophosphine in the reaction mixture. It suggested that the intrinsic viscosity changes would be still higher for very low concentration of phenyl-dichlorophosphine. The experiments confirmed the suggestion completely (Fig. 1), because a maximum in intrinsic viscosity appeared even for samples of copolymers that included unreacted monomers. Such a shape of the intrinsic viscosity curves (Figs. 1 and 2) can be explained if it is assumed that during copolymerization there is some degradation of macromolecules and also a simultaneous formation of new molecules of low degree of poly-merization. This was confirmed by determinations of molecular weight of methyl methacrylate–phenyldichlorophosphine copolymer by the light-scattering method.[7]

Barb[5,6] and Marvel[8,9] showed that degradation of copolymers formed in the semivinyl copolymerization of styrene with sulfur dioxide occurs very easily. As methyl methacrylate and phenyldichlorophosphine were poly-merized by a bulk method, there could be an increase of temperature in the copolymerization system in spite of thermostating and the small diameter (7 mm.) of the glass ampules. This suggests that an increase of tempera-ture resulting from the exothermic nature of the copolymerization reaction has some influence of changes of the intrinsic viscosity. In this case, the probability of degradation is very high, because in the main chains of co-polymer there are C—P bonds existing which are slightly weaker than the C—C bonds. The very active chlorine atoms existing in macromolecules bonded to phosphorus can also have some influence on the degradation process.

References

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Résumé

On a examiné la viscosité intrinsèque des copolimères de méthacrylate de méthyle (M₁) avec la phényldichlorphosphine (M₂) en proportions moléculaires suivantes: $M_1:M_2 = 1:0.012$, $1:0.026$, et $1:0.062$ en fonction du temps de copolimerisation et on a constaté que pour les produits obtenus, la viscosité intrinsèque s'augmente au debut, passe par un maximum et puis se baisse. Tels changements de la viscosité intrinsèque on a expliqué au moyen de degradations et relative faible de reactivité de comonomère phosphoroorganique.

Zusammenfassung

Die Viscositätszahl der Mischpolymerisate vom Methylmethacrylat (M₁) mit Phenyl-dichlorophosphin (M₂) im Molverhältnis $M_1:M_2 = 1:0.012$, $1:0.026$, und $1:0.062$ wurde in Abhängigkeit von der Zeit der Mischpolymerisation untersucht und es wurde fest-gestellt, dass die Viscositätszahl der erhaltenen Produkte anfangs steigt und später nach dem Erreichen des Maximums sinkt. Derartige Veränderungen der Viscositäts-zahl werden durch die Degradation und kleine relative Reaktionsfähigkeit des phosphor-organischen Mischmonomers erklärt.