

# Investigations on Methyl Methacrylate Polymerization Course in the Presence of Petroleum Asphalt Group Components

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## Synopsis

Methyl methacrylate photopolymerization was investigated in the presence of group components isolated from road asphalt D35. It was observed that all asphalt group components, particularly asphaltenes, had an inhibiting influence on the degree of MM conversion. Based on results of measurements of the viscosity-average relative molecular mass of the fractions isolated from the reaction products, we can make a hypothesis that asphaltenes perform a role as polyfunctional chain conveyors.

## INTRODUCTION

One of the ways of improving asphalt properties is to prepare them with polymers. Numerous by-products and waste products obtained during industrial polymer production can be also used for this purpose.<sup>1,2</sup>

One of the methods of asphalt property improvement is monomer polymerization conducted directly in asphalt medium. In chemical structure, asphalt is a complex mixture of organic compounds with aliphatic, cyclic, and heterocyclic hydrocarbons. This mixture contains three fundamental groups of compounds: oils, resins, and asphaltenes, which are different in chemical character, molecular mass, and physical properties. Condensed and aromatic degrees of the compounds present in asphalt increase from oils to asphaltenes.<sup>3</sup> It has been observed that, in asphalt structure, there are also present free radicals stabilized with a delocalized bonding system in aromatic and heterocyclic structures. The highest degree of stable free-radical concentration is characteristic of asphaltenes, no radicals are present in oils.<sup>4</sup> The chemical modification of a asphalt requires considering the interaction of these substances. The available literature does not often deal with such reaction mechanisms, and the information presented is not generally of a utilizable character. Such treatment of a subject results from the great complexity of asphalt's structure, which makes it difficult to adopt a suitable research methodology. Some works point to the inhibiting influence of asphalt, particularly asphaltenes, on the polyreaction course.<sup>5-8</sup>

The aim of our investigations was to determine the influence of particular group components separated from petroleum asphalt on the course and products of radical polymerization.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MM) was chosen as a monomer for the system examined due to its ability to dissolve asphalt substances and due to the possibility of choosing selective dissolvents and precipitators. The practical aspect of this substrate's selection for asphalt property modification was the chance of utilization of useless wastes formed during the industrial production of MM. These wastes contain about 30% monomer.

Group components were isolated from road asphalt type D35 due to its average properties and group component content in comparison with other asphalts produced in Poland. The properties of asphalt applied in the investigations are the following: softening point (°C) according to the Pand K method, 51; fragility point (°C) according to Fraas, -6; penetration at 25°C (°P), 37; ductility at 25°C (m), > 1; group component content (wt %): asphaltenes, 17.9; resins, 40.3; oils, 41.8

Particular group components were isolated from asphalt by means of the Lysichina method according to the only Polish standard of group analysis. This method makes use of the difference in solubility of the particular components in acetone and benzene.

### Method of Synthesis

Photopolymerization without a sensitizer additive was applied as a simple way of conducting polymerization in the presence of asphalt group components. The advantage of this method is also a lack of any additives, making the reaction course examining impossible.

Polymerization was carried out inside a quartz test tube by initiating the reaction with a mercury lamp. The corresponding asphalt group component was dissolved in benzene, mixed with MM and subjected to ultraviolet irradiation.

The polymerization product was precipitated by methanol and then filtered and dried. The efficiency of the product was determined, and on this ground the degree of the monomer conversion was calculated. The product composition obtained was also calculated; it was different from the substrate composition, as MM only partly reacted.

### Investigation of the Products

It was difficult to work out a uniform method of selection for compositions containing particular group components of asphalt as the molecular masses of the applied substrates were considerably different. Our requirements were met by joining the technique of selective precipitation with selective elution. In this method, cyclohexane was applied as a selective precipitator PMM from the composition solution in benzene, and carbon disulfide was used for selective elution of the asphalt group component. It was observed that the fraction separated as PMM had a dark, unelutriated coloring. As this pointed to the presence of asphalt substances in the fraction, it was

decided to continue polymer fractionation on the dark and light fractions according to coloring by the benzene-methanol system.

The conventional softening point and average molecular mass were also determined for the products obtained. This temperature was determined by heating the product in a thin-walled capillary tube in the established way. The temperatures were read twice, first when the softening effect could be observed and then when the whole product melted.

The average molecular masses of the fractions examined were determined by means of a viscosity method in an Ubbelohde viscometer at 25°C, applying benzene as a solvent. In the calculations of molecular mass according to the Mark-Houwink equation, the approximation was adopted using the parameter values of this equation concerning PMM solutions in benzene.<sup>9</sup> The application of this approximation was possible because we did not aim to determine absolute values but only to make a comparative analysis.

## RESULTS AND DISCUSSION

Investigating the MM polymerization course in the presence of asphalt group components, it was decided to determine the influence of particular group component contents on the degree of monomer conversion. All the other reaction conditions were kept the same: the distance from radiation source, 0.15 m, and polymerization time, 15 h. The content of asphalt group components in the reaction medium was changed every 5 wt% in the range from 5 to 25 wt%. The results of the investigations for MM polymerization course with a different asphalt group component content in the reaction medium are presented in Figure 1. For comparison, the curve showing the dependence for unseparated asphalt was also presented. The presence of asphalt compounds in the reaction medium caused a decrease of the monomer reaction degree. This effect becomes more intense due to an increase of asphalt group component content. The lowest reaction degree in the

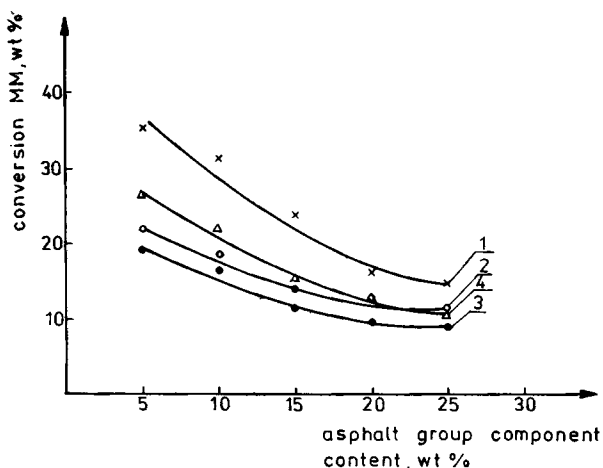


Fig. 1. The course of MM photopolymerization in the presence of asphalt D35 and its particular group components: (1) oils, (2) resins, (3) asphaltenes, and (4) asphalt D35.

presence of the same amount of asphaltenes, resins, and oils is obtained for asphaltenes. For the most active asphaltenes in the polymerization course, an additional series of experiments was carried out in which the time of irradiation was the parameter differentiating these particular experiments. The other conditions were the following: asphaltene contents, 10 wt%, and distance from irradiation source, 0.15 m. Figure 2 presents these results as well as the analogous dependence for unseparated asphalt.

The results presented show that making the time of irradiation longer limits the inhibiting action of asphalt compounds on the polymerization course. If the whole amount of monomer is to react in the case of 10 wt% asphaltenes present in the reaction medium, irradiation of 100 h is necessary; in case of the same amount of asphalt, 80 h. The fractionation composition examined as described allows for the statement that the products of MM polymerization carried out in the presence of particular asphalt group components are not an entirely physical mixture of the applied component and polymer, but they also contain a product of their chemical bonding. The residue after these two isolation operations and the dark fraction isolated from the polymer may be regarded as such a product. The results of measurements for the softening point of the products are presented in Table I.

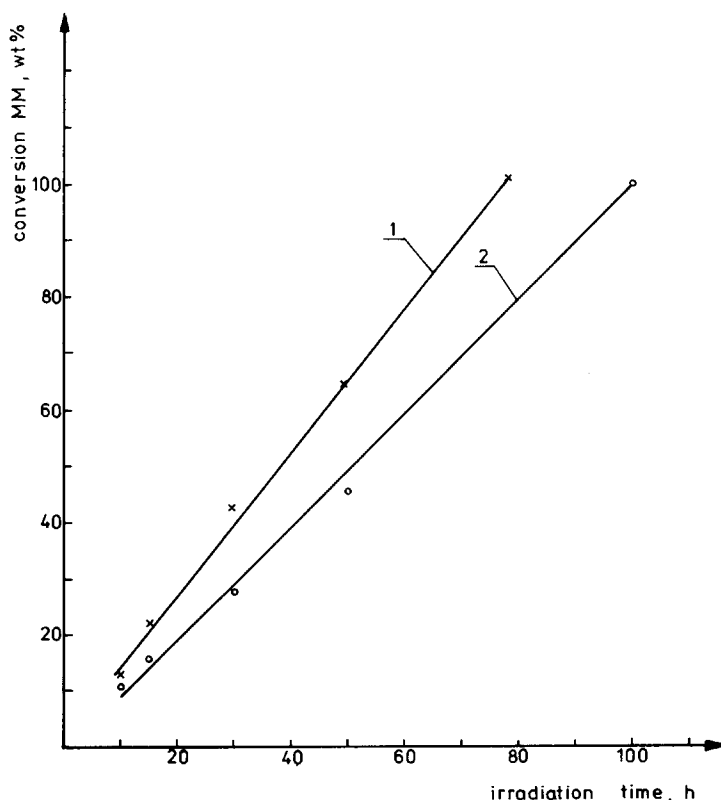


Fig. 2. The influence of irradiation time on the course of MM photopolymerization in the presence of asphalt D35 and asphaltenes isolated from it: (1) asphalt D35, (2) asphaltenes.

TABLE I  
Softening Point of Compositions Containing Oils, Resins, and Asphaltenes

	Initial content of asphalt component (wt%)	Conventional softening point (°C)
Oils	5	225-267
	10	201-238
	15	192-224
	20	185-220
	25	176-218
Resins	5	178-210
	10	140-173
	15	133-151
	20	130-147
	25	125-138
Asphaltenes	5	
	10	
	15	> 300
	20	
	25	

The temperature (determined in this way) for PMM synthesized in analogous conditions to the examined compositions is 220–242°C. Analyzing the results presented in Table I, it was observed that compositions containing oils and resins have a plasticizing influence on the product properties, and it is particularly significant in the case of these last mentioned. The plasticizing effect increases together with the growth of asphalt component content in the product examined. However, in the case of products containing asphaltenes, a considerable thermal resistance of this component is observed.

Determinations of viscosity-average relative molecular mass were conducted for the light polymer fraction isolated (in the described way) from the products containing resins and asphaltenes. The results given in Table II show that the value of average molecular mass for this polymer fraction increases together with the growth of the initial content of asphalt component in the composition. It is in agreement with an inhibiting role that asphalt group components have the greater inhibitor concentration, fewer centers of growth and this average molecular mass is greater.

The light polymer fraction isolated from products obtained in the presence of asphaltenes has the highest average molecular mass values. This proves that asphaltenes have the strongest inhibiting properties in comparison with other group components of asphalt.

Average molecular mass was also determined for the residue and the dark polymer fraction isolated from the compositions containing asphaltenes obtained in that series of experiments where the irradiation time was the changeable and differentiating parameter. The results were given in Table III.

The residue and dark polymer fraction is most probably the product of polymer macroradical inactivation by stable free radicals of asphalt components. The different solubility of these fractions probably results from

TABLE II  
Average Molecular Mass of the Light Polymer Fraction Isolated from Compositions  
Containing Asphaltenes and Resins

Initial content of asphalt component, (wt%)	Asphaltenes					Resins				
	5	10	15	20	25	5	10	15	20	25
Average molec- ular mass $M_p \times 10^{-4}$	9.6	10.7	11.1	13.2	15.3	7.7	8.8	9.6	10.5	11.8

participation of different polymer segments and those of asphalt in their structure.

The average molecular mass increase of the residue for compositions with different irradiation time might point to the fact that asphalt compounds are polyfunctional chain transfer agents, which is revealed at longer reaction times. The dark polymer fraction, however, is a product more like polymer and thus a greater dose of an agent initiating polymerization causes a decrease of average molecular mass.

### CONCLUSION

It was observed that all asphalt group components had an inhibiting influence on the course of MM polymerization. The inhibiting effect was slightest if oils were present in the reaction medium and strongest in the case of asphaltenes. This confirmed our assumption that the inhibiting properties of asphalt as a whole are dependent upon asphaltenes. It can be explained by their structure and greater concentration of stable free radicals. The degree of monomer conversion decreases, together with an increase of asphalt component amount in the reaction medium. It was also observed that making the time of polymerization longer limited the inhibiting action of asphalt components. This can be explained by the fact that asphalt was losing its reaction activity as the reaction proceeded. The results of average molecular mass measurements for fractions isolated from the examined products allow us to assume that asphalt components play their role at the stage of polymer macroradical inactivation. Fractionation of composition does not result in their complete separation into polymer and corresponding group component, in the amounts corresponding to the cal-

TABLE III  
Average Molecular Mass of Residue and Dark Polymer Fraction Isolated from Products  
Containing Asphaltenes (Series with Changeable Irradiation Time)

Average molecular mass $M_p \times 10^{-4}$	Irradiation time				
	10	15	30	50	100
Residue	8.4	9.8	12.7	17.5	25.1
Dark polymer fraction	81.0	67.0	50.0	32.0	27.0

culated composition of the product. The residue obtained is insoluble in selective asphalt and polymer solvents, so it can be assumed that the residue is the product of asphalt reaction with monomer having the character of graft copolymer.

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Received May 6, 1985

Accepted July 6, 1985