Polymer Bulletin 19, 149–154 (1988)

Polymer Bulletin

Complex formation in the template polymerization of methacrylic acid along poly(2-vinylpyridine)

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SUMMARY

The polymerization of methacrylic acid in presence of poly/2-vinylpyridine/ of different molecular weight was investigated. The resulted complex has been separated and analysed by elemental analysis and UV spectrometry. The kinetics of complex formation was examined by means of nephelometric analysis and determination of acid groups. The results obtained show that the complex formation rate does not depend visibly on the degree of polymerization of the template due to the template polymerization.

1. Introduction

The template polymerization process arouses greater and greater interest. The best known example of this process is the polymerization of methacrylic acid in the presence of poly/2-vinylpyridine/. Some papers /1-6/ have recently dealt with this subject including the effects of template concentration /1/, initiator concentration /2/, monomer concentration /3/, template tacticity /4/, temperature /5/ and solvent /6/. These studies have allowed to propose a mechanism of the process and to describe its kinetics.

It seems, however, that despite so thorough studies, some questions have not been fully understood as yet. This concerns the effect of the molecular weight of template on the process as well as the formation of poly/methacrylic acid/ without a complex being

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formed simultaneously with the template polymerization. These questions are the subject of the present study. The template polymerization has been carried out using fractions of poly/2-vinylpyridine/. The resulted complex has been separated and analysed.

2. Experimental

2.1. Fractionation

In order to produce template fractions, a fractional precipitation of poly/2-vinylpyridine/ was carried out from a methanol solution using water as non-solvent. Molecular weights of the fractions were determined by viscosimetry at 25°C in methanol with the use of the relationship:

$$[\eta] = 11.3 \times 10^{-5} M^{0.73}$$

Fractions with the following molecular weights were used for the experiments: 231, 375, 693, 889 and 1431.

2.2. Polymerization

The polymerization was carried out in a round-bottom flask provided with a stirrer, a reflux condenser and input and output for nitrogen, using dimethylformamide /DMF/ as solvent and azobisisobutyronitrile AIBN as initiator. The reaction was performed at a temperature of 60°C. The monomer concentration was 0.23 mol/l in all the cases; the template concentration was 0.1 mol/l and that of initiator 0.015 mol/l.

2.3. Methods of Analysis

a/ The extent of monomer conversion to polymer due to the polymerization without template was measured by bromometric titration of double bonds.

b/ The number of acid groups was determined in the filtrate after filtering off the complex precipitated as in /c/. The filtrate was titrated with a 0.05 n NaOH solution against phenolphthalein. This method allows to find all the acid groups in the unconverted methacrylic acid and in th non-complexed poly/methacrylic acid/. The difference between the initial measurement und that carried out after time t gives the amount of acid combined with the template /conversion into complex/, which allows to prepare a calibration diagram.

c/ The amount of the polymer complex formed was determined by the nephelometric analysis. A sample of the reaction mixture was diluted with ethyl alcohol in ratio 1:1. It was found on the basis of separate tests that under these conditions, a stable sol is formed from the complex of poly/2-vinylpyridine/ and poly/methacrylic acid/; its concentration can be determined by measuring light absorption in a photocolorimeter from Elmed, using a 690 nm filter. The complex concentration was found from the calibration diagram, and hence the extent of conversion of methacrylic acid into a complex with the template.

d/ The concentration of poly/2-vinylpyridine/ was measured by UV spectrometry /7/, using DMF as solvent. The measurements were taken for concentrations of the magnitude 10^{-4} mol/l at a wavelength of 267 nm. The useability of the Beer law was confirmed previously and a standard straight line was prepared.

e/ The composition of the separated complex was examined by the method of elementary analysis.

3. Results and Discussion

In order to verify the accuracy of the methods and to compare the results with the literature data, polymerization of methacrylic acid without the template was carried out. The extent of conversion was determined by the bromometric method as described in /a/. The results are given in Fig. 1, in the system used for classic polymerization, i.e.: -ln/1-a/ versus time t. As is seen, the polymerization proceeds according to the equation V = K/M/x $/I/^{1/2}$, taking into consideration that the small period of activation is brought about probably by the rest of unremoved oxygen. The calculated value of K is 2.72×10^{-4} $mol^{1/2}s^{-1}$. This value refers to the temperature used by us. i.e. 60°C and is similar to the value $3.0\times10^{-4}mol^{1/2}s^{-1}$ calculated for this temperature from the equation K = exp/21.5 - 82×10^{3}/RT/ given in paper /5/.

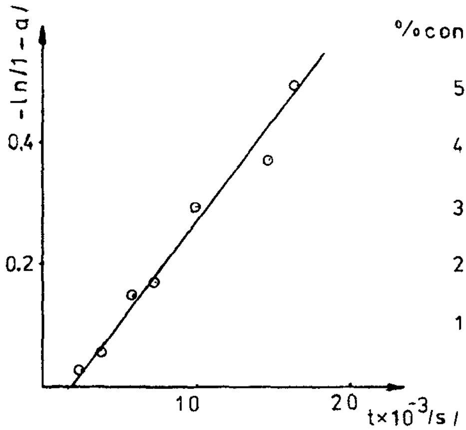

Figure 1. Plot of -ln/1-a/ vs. time for blank polymerization of methacrylik acid.

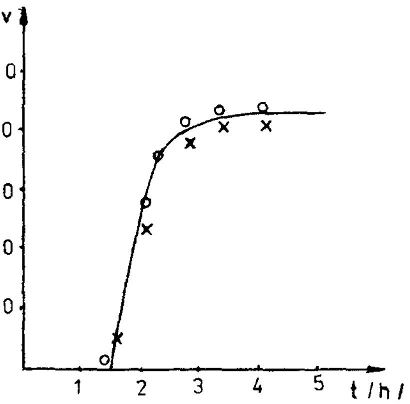

Figure 2. % of conversion of methacrylic acid into complex. x -nephelometric method, o -acid group titration.

The results of the template polymerization are given in Fig. 2. It is worth noting that the used method of complex separation allows to follow the kinetics of complex formation and not the kinetics of the overall polymerization proceeding also beyond the template. The ordinate axis in Fig. 3 show the extent of conversion of the methacrylic acid wihich takes part in the composition of the complex with the template. As is seen, the conversion so calculated reaches a value of about

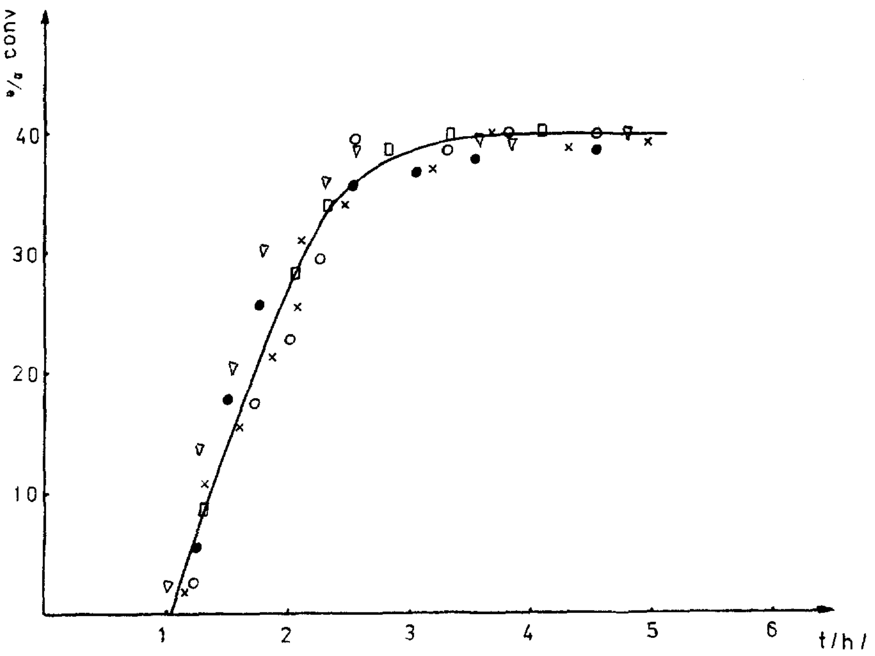

Figure 3. % of conversion of the monomer into complex in template polymerization. Degree of polymerization of poli/2-vinylo pirydine/ /template/: ▽ - 231, × - 375, ● - 693, □ - 889, ○ - 1431.

42% and then does not change. This is in agreement with the excess of monomer used with respect to the template and, on the other hand, with the assumed equimolar complex composition. This assumption was additionally confirmed by elementaly analysis of the separated complex composition /found N = 7.4%, calculated for the equimolar composition N = 7.3%/.

It follows from the initial composition of the monomer-template mixture that the maximum amount of poly/methacrylic acid/ corresponds to a conversion of 44% at the assumed complete "filling" of the template. It results from the above facts that recombination of the radical of filled template with the macroradicals of the homopolymer formed beyond the template is hardly probable to occur. It amounts to a low value of the constant of cross-termination.

In addition, one can state that the relative initial rates of the template polymerization /the ratio of the template polymerization rate to the polymerization rate without template/ are within 3.2 - 3.5, which is slightly lower value than that given in paper /1/.

It is seen from the results given in Fig. 3 that the complex formation rate due to the template polymerization does not depend visibly on the polymerization degree of the template within the range under study. This semms to show that the critical length of macroradicals adsorbed by the template is much lower than the corresponding template with the polymerization degree 231.

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Accepted November 15, 1987 C