require molecular weights well over 10^6. It is therefore at least plausible that $\Phi_{(\theta)}$ might behave normally.

Acknowledgment. The authors would like to acknowledge technical assistance from Mr. P. M. Toporowski.

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Some Peculiarities of Thermal Polymerization of Styrene in Chloroform–Acetone Mixtures

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Received March 5, 1974

ABSTRACT: In this study some peculiarities in relation to the kinetics and especially the chain transfer reactions of the thermal polymerization of styrene in chloroform–acetone mixtures have been investigated. It has been found that the values of $1/\bar{P}_n$, the transfer constant for the solvent, k_t/k_p^2, and the fractional rate depend on the concentration of solvent. These anomalies are explained by the formation of complexes among the components of the polymerization system. Thereby the effect of the polarity of the medium must not be neglected.

The problem concerning the effect of medium on the rate and mechanism of polymerization has not been solved yet. This is due to the fact that the quantity of available convincing experimental data or theory is not sufficient.

The solvent affects the polymerization rate especially because of its chemical character, polarity, and viscosity.

The effect of chemical character of a solvent manifests itself in the formation of complexes (solvates) among the solvent and other components of the polymerization system (specific solvation). These complexes contain secondary bonds. Moreover, the autoassociation of particles may also have an influence on the polymerization rate.

The reactivity of polymer radicals may be influenced not only by the solvation of an atom with an unpaired electron but also by the interaction of other atoms and functional groups of radical with solvent. The polar structure of the radical may also influence its reactivity.[1]

There are only a few cases in which the effect of the polarity (nonspecific solvation) of the medium on the overall rate as well as the rates of individual elementary processes of radical polymerization can be clearly observed. Together with the effect of polarity the influence of specific solvation can often be observed.

The analysis of literature data shows[1-16] that according to the character of the solvent, monomer, and polymer radical one or another type of complex can prevail and affect the kinetics of polymerization. Complexes usually reduce the reactivity of polymer radical and monomer[1-5,15] but there are cases in which the reactivity increases.[4,6-15] The character of the interaction between a growing radical and medium is not quite clear.[13]

In several cases a binary system monomer–solvent is not enough to obtain full information on the effect of solvent on k_i, k_p, k_t, R_p, and C_s (transfer constant of solvent).

The literature is short on data concerning the change of k_i, k_p, and k_t, and there are few data on the variation of R_p and C_s in binary mixed solvents.

The study of polymerization kinetics in a binary mixed solvent, the composition of which may vary, is advisable. In this case the concentrations of different solvate forms also vary. Such investigations are necessary for the explanation of the effect of solvent on the reactivity of monomer or polymer radical.

This work has been undertaken in order to study some peculiarities concerning the kinetics and mainly the chain transfer reactions occurring in the thermal polymerization of styrene in chloroform–acetone mixtures.

The polymerization of styrene in some commonly used organic solvents has been studied.[15,17-29] The information available on styrene polymerization in solvent mixture is, however, scanty.

The pair of solvents acetone–chloroform was examined for the first time in the radical polymerization of methyl methacrylate and vinyl acetate in a nitrogen atmosphere.[30] This investigation manifest that not only the proportion of both solvents but also other factors affected the transfer reaction in mixtures of solvents. It may be supposed that these factors involve intermolecular interactions, i.e., the interactions among the molecules of solvents as well as the interactions among the molecules of solvents and monomer.

For the polymerization of styrene the value of the transfer constant to chloroform depends on the concentration of chloroform. This holds well for both the polymerization of styrene in chloroform and thermally and by AIBN-initiated polymerization of styrene in a mixture of chloroform with acetone.[31] The observed anomalies concerning the effect of solvent concentration on the value of transfer constant are attributed to the formation of the complexes from the monomer or polymer and solvent eventually from the solvents as well as to the variations of polarity depending on the composition of solution.

All above-mentioned complications could affect the parameters which occur in eq 2 and 4 determining the chain-transfer constants. That is why it is necessary to estimate the values of the ratios k_t/k_p^2 and $R_p/[M]_a^2$ as well as the fractional rate $R_p/[M]_a$. In principle a study of one anomalous kinetic parameter necessitates the study of other kinetic parameters (or the ratio of kinetic parameters) which are connected with the former.

Experimental Section

The purification of styrene, demands on the quality of chloroform and acetone, preparation of reaction mixtures, evacuation and polymerization conditions, isolation of polystyrene from the polymerization mixture, determination of the number average molecular weight from intrinsic viscosity, and all other procedures used were described elsewhere.[31] In spite of unusual precautions reproducible molecular weights could not be obtained in some cases as shown by Gregg and Mayo.[17] The number of experiments carried out at 60° with each ratio of reactants varied from 2 to 4.

Provided only one solvent, i.e., acetone, was present in the polymerization mixture, the chain transfer constant C_{ac} was calculated by numerical solution of the equation

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_0} + C_{ac}\frac{[S_{ac}]}{[M]_a} \tag{1}$$

or the equation

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p^2}\cdot\frac{R_p}{[M]_a^2} + C_m + C_{ac}\frac{[S_{ac}]}{[M]_a} \tag{2}$$

where the kinetic parameters are involved. $[M]_a$ denotes the mean arithmetic value of the monomer concentration (before and after polymerization).

If two solvents were present in the polymerization mixture, we kept the chloroform and initial styrene amounts in the mixture constant while only the acetone amounts were varied. In this case the chain transfer constant to acetone was calculated by numerical solution of the equation

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_0} + C_{cl}\frac{[S_{cl}]}{[M]_a} + C_{ac}\frac{[S_{ac}]}{[M]_a} = K + C_{ac}\frac{[S_{ac}]}{[M]_a} \tag{3}$$

or

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p^2}\cdot\frac{R_p}{[M]_a^2} + C_m + C_{cl}\frac{[S_{cl}]}{[M]_a} + C_{ac}\frac{[S_{ac}]}{[M]_a} \tag{4}$$

where the kinetic parameters are taken into account. The symbols C_{cl}, C_{ac}, $[S_{cl}]$, and $[S_{ac}]$ stand for the transfer constant to chloroform, transfer constant to acetone, chloroform concentration, and acetone concentration, respectively.

According to the literature[24] the value of $1/\bar{P}_0$ equals 1.01×10^{-4}. In our experiments the value of $1/\bar{P}_0$ was found to be 1.064×10^{-4}, 1.078×10^{-4}, and 1.198×10^{-4}.

The possibility of determining the value of ratio k_t/k_p^2 for thermal polymerization in solvent where transfer reactions to the solvent occur[32] without any initiator[33] has been proved. In our case the ratio k_t/k_p^2 is calculated from eq 2 and 4, using from ref 33 the value $C_m = 8.5 \times 10^{-5}$.

Results and Discussion

Thermal Polymerization of Styrene in Acetone. For the thermal polymerization of styrene at 60° in the presence of small amounts of acetone, $1/\bar{P}_n$ does not increase proportionally with $[S]/[M]_a$ (Figure 1) in contrast to the polymerization of styrene in other solvents. The complications also appear in the relationship between the transfer constant to acetone and the concentration of acetone (Figure 2, curve 1). C_{ac} varies from 17.95×10^{-5} for the concentrations of acetone of 7.45 mol % to 0.30×10^{-5} for 44.41 mol % of acetone. According to ref 17 the value of this transfer constant is in the interval from 0 to 3×10^{-5} or it is lower than 5×10^{-5}. The authors[17] have calculated this transfer constant according to eq 1 but they do not state for what concentration range they have obtained C_{ac}. Our experiments at medium (44.41–61.11 mol %) and higher (79.97–82.58 mol %) concentrations of acetone[31] confirmed these literature data.

In order to explain the anomalies concerning the dependence of $1/\bar{P}_n$ or C_s on the concentration of solvent, we must take a few factors into consideration. We should like to pay attention and discuss in this paper the complex for-

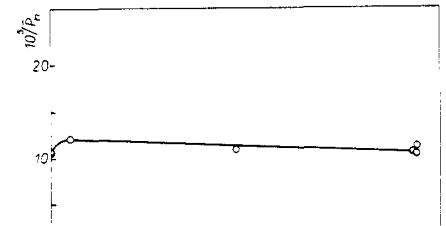

Figure 1. Determination of the acetone chain transfer constants in thermal polymerization of styrene at 60°; [S] = increasing acetone amount in moles; $[M_a]$ = amount of the monomer as arithmetical average value of the initial (0.0348 mol in each experiment) and final quantity.

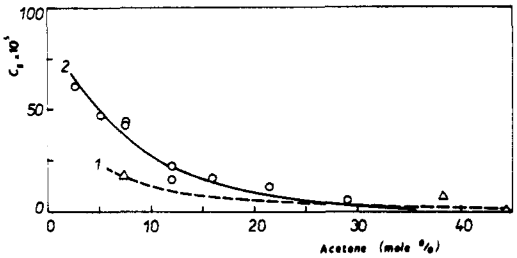

Figure 2. Acetone chain transfer constants (estimated by eq 1 or 3) for the thermal polymerization of styrene in acetone (1) and chloroform–acetone mixture (2) as a function of acetone concentration at 60°.

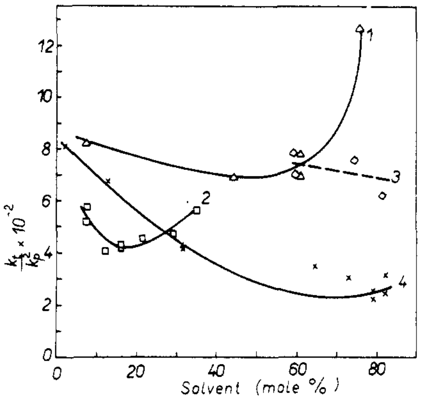

Figure 3. k_t/k_p^2 for the thermal polymerization of styrene as a function of solvent concentration at 60°: (1) in acetone; (2) in chloroform–acetone mixture as a function of acetone concentration; (3) in chloroform; (4) in acetone–chloroform mixture as a function of chloroform concentration.

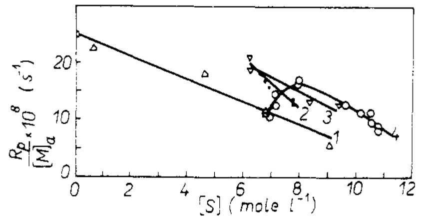

Figure 4. Fractional rates of thermal polymerization of styrene as a function of solvent concentration [S] at 60°: (1) in acetone; (2) in chloroform–acetone mixture as a function of acetone concentration; (3) in chloroform, and (4) in acetone–chloroform mixture as a function of chloroform concentration.

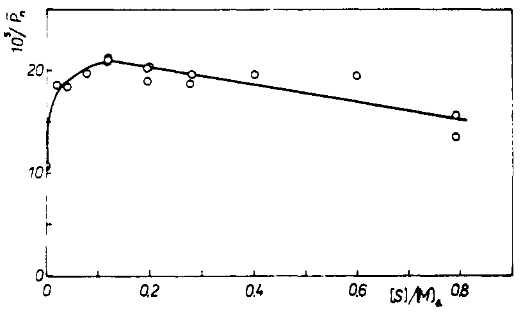

Figure 5. Determination of the acetone chain transfer constants for the thermal polymerization of styrene at 60° in a chloroform–acetone mixture; [S] = increasing acetone amount in moles; $[M_a]$ = amount of the monomer as arithmetical average value of the initial (0.0348 mol in each experiment) and final quantity. Chloroform amount is constant and equal to 0.0496 mol.

mation, the values of the ratios k_t/k_p^2 and $R_p/[M]_a^2$ which appear in eq 2, and the polar effect.

The most plausible explanation of the anomalies concerning the change of the values of $1/\bar{P}_n$ and C_{ac} with the concentration of acetone consists in the idea that the growing polystyrene radical forms a complex with acetone and the reactivity and stability of this complex determines whether $1/\bar{P}_n$ and C_{ac} increase or decrease. Really, a number of authors[15,18,20,21,25,34] are of the opinion that the growing polystyrene radical forms a complex with solvent.

If the chain ending changes, a change in the ratio k_t/k_p^2 may be expected. It can be seen from Figure 3, line 1, that the values of the ratio k_t/k_p^2 decrease and subsequently increase with the concentration of acetone (from 7.45 to 75.82 mol %). This is in agreement with the changes of $1/\bar{P}_n$ and C_{ac} in this concentration region (this paper and ref 31).

The similar dependence of $1/\bar{P}_n$, C_{ac}, and k_t/k_p^2 on the concentration of acetone agrees with eq 2. The dependence of the fractional rate $R_p/[M]_a$ with the concentration of solvent [S] (Figure 4, line 1) is below a horizontal line.

In this paper the values of the overall rate R_p for pure thermal polymerization at 60° vary from 2.08×10^{-6} to 2.36×10^{-6} mol l.$^{-1}$ sec^{-1} and are comparable with the values found in literature, e.g., 1.9×10^{-6},[35] 2.00×10^{-6}, 2.47×10^{-6},[36,37] 2.20×10^{-6},[38] and 2.42×10^{-6} mol l.$^{-1}$ sec^{-1}.[27]

Thermal Polymerization of Styrene in Chloroform–Acetone Mixture. The Amount of Acetone Varies. For the thermal polymerization of styrene at low concentrations of acetone the described anomalies (manifesting themselves in the dependence of $1/\bar{P}_n$ on $[S]/[M]_a$ and the dependence of C_{ac} on the concentration of acetone) are more distinct in a chloroform–acetone mixture provided acetone is present in low concentrations too (Figure 5; Figure 2, line 2). It may be expected that the complexes formed in the presence of chloroform and small amounts of acetone contribute much more to the increase in the reactivity of polystyrene radical with respect to the transfer reactions with acetone than they would do only in the presence of small amounts of acetone.

It is obvious from Figure 3, line 2, that the values of the ratio k_t/k_p^2 are close to the values of this ratio found in the literature for the polymerization of styrene at 60° (from 760 to 935 mol l.$^{-1}$ sec)[25,39,40,41] provided the concentrations of acetone are low (under 20 mol %). With increasing concentration of acetone (over 20 mol %) the value of the ratio k_t/k_p^2 again increases.

It follows from these facts that: (a) the styrene–acetone–chloroform mixture of a certain concentration is responsible for the anomalous changes in the values of the ratio k_t/k_p^2; (b) provided the concentration of acetone is below 20 mol % the kinetic ratio k_t/k_p^2 does not bring any more marked increase in the values of $1/\bar{P}_n$ and C_{ac} according to eq 4.

Thermal Polymerization of Styrene in Chloroform. In this case it has been observed at 60°[31] that the relationship between $1/\bar{P}_n$ and $[S]/[M]_a$ is not linear and the value of transfer constant for chloroform C_{cl} and the overall rate of polymerization R_p depend on the concentration of chloroform.

It is obvious from Figure 3, line 3, that at the concentrations of chloroform of 59.44–81.33 mol % the values of the ratio k_t/k_p^2 are in the range of the values quoted in the literature (760–935 mol l.$^{-1}$ sec).[25,39-41] The dependence of the fractional rate $R_p/[M]_a$ with the concentration of solvent [S] (Figure 4, line 3) is below a horizontal line.

Thermal Polymerization of Styrene in Acetone–Chloroform Mixture. The Amount of Chloroform Changes. For this polymerization at 60° it was observed that the relationship between $1/\bar{P}_n$ and $[S]/[M]_a$ was anomalous.[31] Similarly, the value of transfer constant for chloroform C_{cl}, the overall rate of polymerization R_p (less distinctly),[31] and the ratio k_t/k_p^2 (Figure 3, line 4, in more than 30 mol %) vary with the concentration of chloroform.

It is evident from Figure 3, line 4, that the value of the ratio k_t/k_p^2 decreases with increasing concentration of chloroform (up to 73 mol %). Similar low values were also obtained by the thermal polymerization of styrene in chloroform–acetone mixture provided the content of acetone was about 17 mol % (Figure 3, line 2); i.e., the content of chloroform was about 73 mol %. It may be that the complexes of polystyrene radical in the presence of solvent which are responsible for the variation of C_s are also able to reduce the values of the ratio k_t/k_p^2 in this concentration region.

A further increase in the concentration of chloroform (more than 73 mol %, Figure 3, lines 2 and 4) results in an increase of the ratio k_t/k_p^2. A tendency appears to reach the values of the ratio k_t/k_p^2 (760–935 mol l.$^{-1}$ sec) which usually occur in the polymerization of styrene in chloroform.

The fractional rate $R_p/[M]_a$ (Figure 4, line 4) increases and afterwards decreases with increasing concentration of solvent. Some changes in the fractional rate with the concentration of solvent were also observed in the case of the AIBN-initiated polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate in benzene.[42]

Some General Considerations on the Thermal Polymerization of Styrene in the Investigated Systems. The lower concentrations of acetone or chloroform are responsible for the higher values of $1/\bar{P}_n$ (Figure 5 and ref 31) and

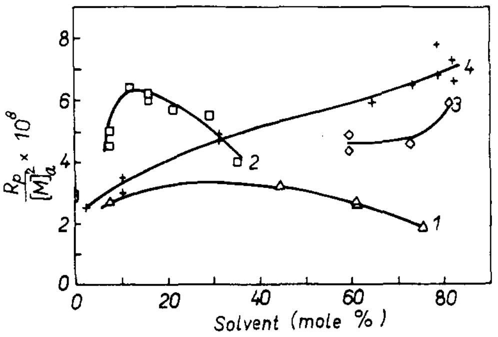

Figure 6. $R_p/[M]_a^2$ for the thermal polymerization of styrene as a function of solvent concentration at 60°: (1) in acetone; (2) in a chloroform–acetone mixture as a function of acetone concentration; (3) in chloroform; (4) in an acetone–chloroform mixture as a function of chloroform concentration.

C_s (Figure 2 and ref 31). The transfer constants are greater at lower concentrations of acetone in the system styrene–chloroform–acetone (Figure 2, line 2) than at lower concentrations of chloroform in the system styrene–acetone–chloroform or styrene–chloroform.[31] It is known that the polarity increases with the dielectric constant and dipole moment of solvent molecules. In our case the order of components according to the dielectric constants (ϵ) and dipole moments (μ) is as follows: acetone, $\epsilon = 21.45$,[43] $\mu = 2.69$;[44] chloroform, $\epsilon = 4.806$,[44] $\mu = 1.15$ at 25°;[44] styrene, $\epsilon = 2.4257$,[44] $\mu = 0.13$.[44] These data are valid at 20° except for the dipole moment of chloroform. The polystyrene radical is relatively unreactive and its reactivity can be strongly influenced by polar effects in the transition state.[20,45] Therefore the polarity of acetone may play a role in the increase of the transfer constants in the system styrene–chloroform–acetone.

With the increase in the concentration of acetone or chloroform the extent of transfer reactions (Figure 2 and ref 31) decreases. This anomaly may be explained by assuming complex formations styrene–solvent, acetone–acetone, chloroform–chloroform (this paper and ref 31), and acetone–chloroform[46] which likely shade the dipole charge of the complex polystyrene radical–solvent.

In this paper the transfer constants have been calculated according to eq 1 and 3 so that they can be compared with the transfer constants calculated by other authors according to eq 1 too. The transfer constants obtained by the use of eq 2 and 4 which take into account the kinetic parameters expressed by the values of k_t/k_p^2 and $R_p/[M]_a^2$ are in agreement with the values calculated according to eq 1 and 3.

The fractional rates are greater in three-component systems (Figure 4, lines 4 and 2) than in the two-component system styrene–acetone (Figure 4, line 1).

It can be seen (Figure 6, lines 1, 2, 3, and 4) that the change in the value of the ratio $R_p/[M]_a^2$ with the concentration of solvent is reversaly in comparison with the change of the values of the ratio k_t/k_p^2 (Figure 3, lines 1, 2, 3, and 4).

Summary

For the thermal polymerization (60°) of styrene in chloroform, acetone, or a mixture of both these solvents the values of $1/\bar{P}_n$ and C_s decrease from high values (at low concentrations of acetone or chloroform) to low values (at medium concentrations of acetone or chloroform) and increase again at high concentrations of acetone or chloroform.

The most plausible explanation of the anomalous change of the values of $1/\bar{P}_n$ and C_s with the concentration of acetone or chloroform consists in the idea that the growing polystyrene radical forms a complex with solvent in the transition state. It is the reactivity and stability of this complex influenced by the polar effect that determines whether $1/\bar{P}_n$ and C_s increases or decreases. Furthermore, the complexes formed among the molecules of solvents may also play a role.

The transfer constants are greater at lower concentrations of acetone in the system styrene–chloroform–acetone than at lower concentrations of chloroform in the system styrene–acetone–chloroform or styrene–chloroform. This is in agreement with the fact that acetone shows a greater polarity than chloroform.

The fractional rates are greater in three-component systems than in the two-component system styrene–acetone.

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Synthesis and Investigation of Poly(aroylene-*s*-triazoles)

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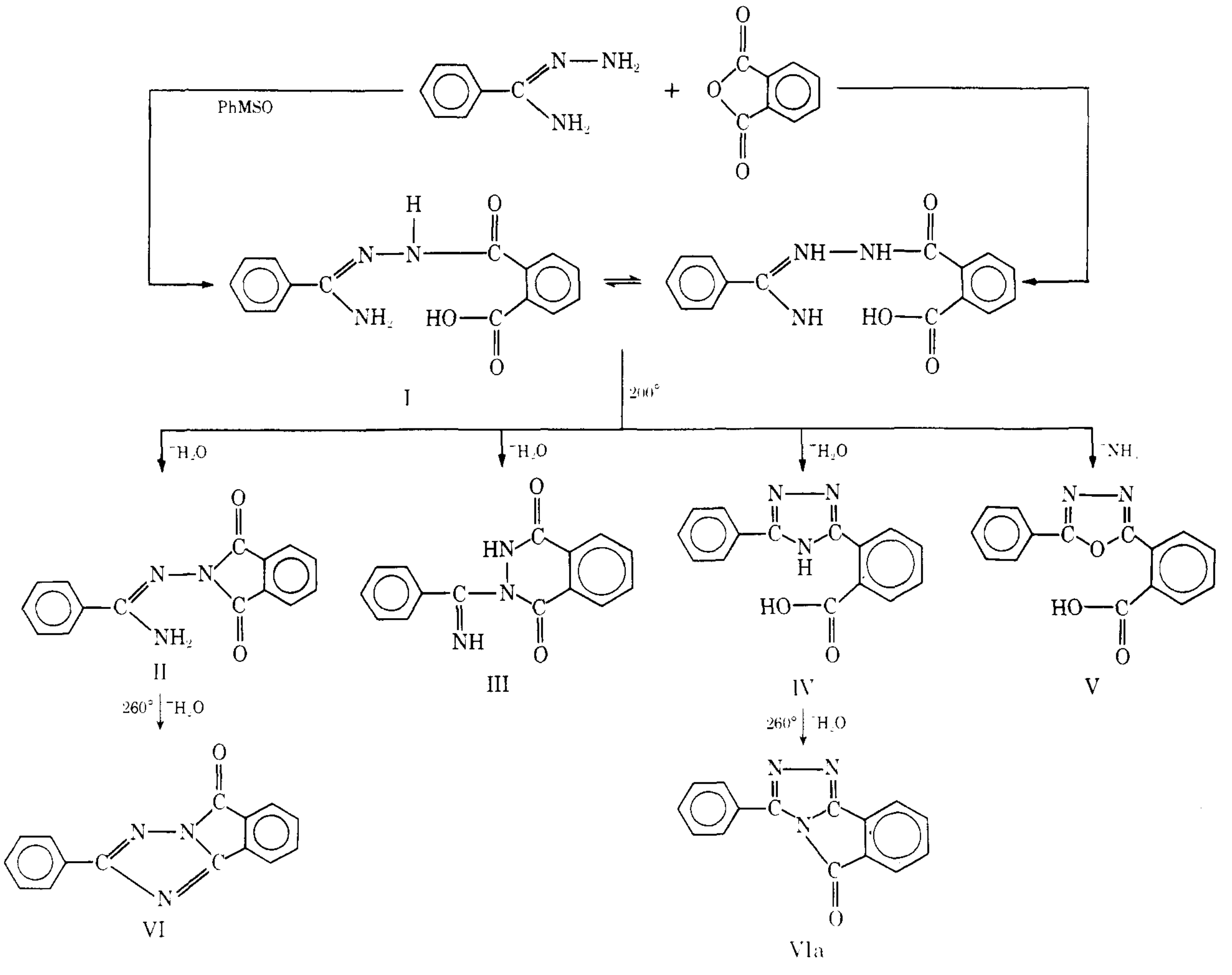
Received June 11, 1974

ABSTRACT: Poly(aroylene-*s*-triazoles), thermally stable "step-ladder" polymers, were prepared by the interaction between bisamidrazones and tetracarboxylic acid dianhydrides using the multi-stage procedure and one-stage polycyclocondensation in poly(phosphoric acid) (PPA). The effect of polymer structure on solubility and thermal stability was investigated.

Recent publications on poly(aroylene-*s*-triazoles), poly(benzoylene-*s*-triazoles),[1] and poly(naphthoylene-*s*-triazoles)[2] prompted us to disclose our independent findings on the preparation of these polymers.[3-6] In contrast with the very well-known poly(aroylenebenzimidazoles),[7] these polymers were discovered in 1968,[3] when we found that solid-state polycyclocondensation of poly(*o*-carboxybenzoylamidrazones) led to the formation of poly(aroylene-*s*-triazoles), but not to poly(*o*-carboxyphenyl-*s*-triazoles).[8] Following investigations carried out by several groups resulted in the preparation of the two general types of poly(aroylene-s-triazoles), poly(benzoylene-s-triazoles) [poly-



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