Role of the Charge-Transfer Complex during the Copolymerization of *N*-Vinylpyrrolidone and Maleic Anhydride

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ABSTRACT: An attempt is made to prove the possibility of synthesizing copolymers of *N*-vinylpyrrolidone (VP) and maleic anhydride (MA) with a kinetically regulated structure of the macromolecule. The influence of the charge-transfer complex (CTC), formed from VP and MA, on the dominating tendency toward alternating copolymerization of the two comonomers is studied. The process is carried out on the following model of interaction: a mixture of VP and MA (molar ratio 1:1) is added at a fixed value of mass flow to the reaction system where VP homopolymerization takes place. The copolymerization is studied under adiabatic and isothermal conditions at different mass flow values. The correlation between the parameters of the adiabatic process and the composition and molecular weight of the copolymers obtained in isothermal conditions at one and the same mass flow value is found. It was found that the decrease of the mixture mass flow to a certain value does not affect the copolymers composition and the dynamic of the temperature change in the adiabatic regime. The decrease of mass flow below that threshold leads to increasing the VP content in the product and to enhancing the rate of temperature increase in the adiabatic regime. The analysis of these data shows that it is quite possible to maintain a definite content of MA in the system, at which the dominating tendency toward alternation is disturbed. The results allow us to clarify the role of CTC in the VP/MA copolymerization process and to give a positive answer to the question: Is it possible to synthesize copolymers with a kinetically regulated structure of the macromolecule?

Introduction

Studies on the initiated by radical copolymerization of *N*-vinylpyrrolidone (VP) and maleic anhidride (MA) are reported by many authors.[1-5] They show that the copolymers obtained consist of equimolar amounts of the two comonomer units, which are alternatingly arranged along the macromolecular length. Such a copolymer is formed independently of the initial ratio of the comonomers.[4] The dominating tendency toward alternation is due[1,5] to the charge-transfer complex (CTC) of VP and MA, which takes part in the reaction process as an independent monomer. The complex is attached to the growing polymer chain[5] anticipated with respect to the free VP and MA.

CTC is obtained spontaneously when mixing VP and MA (the solution is green):

$$\mathrm{VP} + \mathrm{MA} \rightleftarrows \mathrm{CTC} \qquad (1)$$

The aim of the present study is to answer the question, is it possible to synthesize a nonalternating copolymer of VP and MA? And if it is, under what condition? The attempt to realize such synthesis needs to clarify the reasons for anticipating incorporation of CTC into the growing macrochain and to find out an efficient way to compensate it.

In general, the reasons for the anticipating attachment of CTC could the following: The CTC has a high equilibrium constant. So, the equilibrium (1) is to the right to such an extent that the equilibrium concentrations of VP and MA are insignificant. The affinity of CTC toward the growing macroradical is several orders of magnitude higher than that of VP and MA.

The first assumption, a high equilibrium constant (K) of CTC

$$K = \frac{[\mathrm{CTC}]}{[\mathrm{VP}][\mathrm{MA}]}$$

cannot explain the tendency toward alternation, which is observed when there is a considerable excess of VP with respect to MA. Unfortunately, we could not find any data about K in the literature. According to Kokubo[1] a spontaneous alternating copolymerization (with CTC participation) takes place with an equilibrium constant of the complex of the order of 10^{-1}. At K values of the order of 1–5, alternating copolymerization with CTC participation is possible only by an ionic mechanism while at higher values it does not take place at all. Therefore, the alternating copolymerization in our case takes place in a mixture of commensurable amounts of CTC, VP, and MA. Obviously the growing macromolecules selectively react with CTC and ignore VP and MA. This fact logically leads to the assumption that CTC affinity toward the macroradical is much higher than that of VP—by several orders of magnitude. So, the synthesis of nonalternating copolymer presumes the establishment of reaction conditions under which the difference in affinity could be compensated. This could be achieved by a relative decrease of MA concentration in relation to VP concentration. The model of interaction, allowing maintenance of a very low CTC concentration for long period of time, suggests adding a VP/MA mixture (molar ratio 1:1) at a fixed mass flow to the reaction system where homopolymerization of VP takes place. The added amount of MA per unit time is so small compared to the available amount of VP that it is practically completely involved in the formed complex (according to equilibrium). In dependence of the mass flow value of the VP/MA mixture (1:1) (provisionally called CTC) two effects are possible: (1) An alternating copolymer is formed—this is an indication that added amount of CTC per unit of time is greater than the amount involved in the product for the same time. So CTC is generated in the reaction system. (2) A nonalternating copolymer is formed (with a greater amount of VP units)—this is an indication that the added quantity of CTC per unit time is smaller than the amount that would by involved in the product for the same time. In these cases, a very low, unchangeable (stationary) concentration of the reagent (in our case CTC) is established. The alternating function periodically is interrupted in the reaction volume elements, which gives a chance for free VP to incorporate into the growing copolymer chain.

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If the second effect is possible and real, by controlling the mass flow value of the VP/MA mixture (1:1) the structure of every single copolymer macromolecule can be regulated by effective agitation. Our study is an attempt to prove this possibility. The assumptions made are confirmed experimentally by the described model of interaction. The effective rate of copolymerization at different mass flow values of CTC is presented by the rate of heat release (heat power) of the process. The heat power was expressed by the rate of temperature increase in the reaction medium, determined in the adiabatic regime. The composition of the copolymer obtained under isothermal conditions at a fixed value of CTC mass flow was used as a measure of the degree of participation of the free VP in the copolymerization process. The correlation between the influence of the mass flow on the effective rate of copolymerization and on the composition of the copolymer, obtained under isothermal conditions, was studied. The correlation allows us to determine the threshold of mass flow decrease, below which a stationary concentration of CTC is established in the reaction medium.

The data obtained allow us to make a conclusion about the role of CTC in the copolymerization of VP and MA. The experimental results reveal a possibility for synthesizing copolymers, in which macromolecules are characterized with alternatingly arranged long, statistically equal sequences of VP units and single units of MA. The copolymers obtained are analogous in physical properties to poly(vinylpyrrolidone) and possess a chemical activity in mild conditions and a very good perspective for practical application.

Experimental Section

Materials. Syntheses were carried out by using the following substances: VP (Fluka) after distillation at 73–75 °C (2–3 mmHg) for removing the stabilizer; MA (mp 52 °C) after redistillation in chloroform; azobis(isobutyronitrile) (AIBN, Merck) as initiator, after recrystalization in ethanol; benzene and toluene (Lachema-Brno) as solvents (moisture content below 0.05 wt %); diethyl ether (Krasnaya Zvezda-Bulgaria) as a precipitator; nitrogen gas, for an inert atmosphere of the reaction medium.

Apparatus. A 0.7-L reactor is equipped with a heating–cooling system, through which a heat-transfer fluid is run. The heat-transfer fluid is conditioned in a thermostat. Its heating is achieved in a stepwise fashion, regulated by a contact thermometer, placed in the thermostat; the cooling is done by a water serpentine (in the thermostat), to which cold water is let through by an electromagnetic valve. The valve is switched on by another contact thermometer, placed in the reaction medium. Nitrogen (at ambient temperature) is purged through the reaction medium. Increasing the gas flow makes it possible to compensate the rapid enhancement of the heat realize rate. The optimized work volume of the reactor and the good isolation characteristics allow us to maintain adiabatic (with negligible heat loss) and isothermal (with temperature precision ±0.5 °C) conditions.

The reactor is also fitted with a reflux condenser (with a hydraulic gate and a turbine stirrer, permitting a change in rotation speed).

Switching from the isothermal to the adiabatic regime (interrupting the heat-transfer fluid flow, the inert gas flow, and the cooling water in the reflux condenser) can be done with only a single act.

Methods of Synthesis. 1. Homopolymerization of VP and Copolymerization of a VP/MA Mixture in Molar Ratio 1:1. The VP solution, previously prepared, or the mixture of the monomers in benzene is heated up to 76 °C in the reactor, switched on to work in an isothermal regime. The initiator is added as a 5 wt % benzene solution. A constant rate of the stirrer is maintained. The temperature is fixed at 76 ± 0.5 °C. The reactions are interrupted after equal time intervals from the beginning of the process but before the gel effect has taken place. The solution is cooled by adding equal volumes of cold benzene. The polymer is isolated by precipitation in diethyl ether.

The copolymerization of VP and MA in molar ratio 2:1 proceeds in the same manner. At every hour of the process time a test sample is withdrawn from the reaction medium for analyzing the composition of the product obtained and determining the amount of unreacted MA.

2. Polymerization of VP Accompanied by Addition of CTC Mixtures with Different Concentrations and Equal Volume Flow. The addition of a CTC mixture with different concentrations and equal volume flow is equivalent to a different mass flow of CTC. (i) Under isothermal conditions. A previously prepared mixture of VP in benzene is heated up to 76 °C in the reactor switched on for the isothermal mode. The initiator dissolved in benzene is added to the reaction medium. After 10 s the introduction of CTC is begun (a mixture of VP and MA in molar ratio 1:1), dissolved in benzene to a corresponding concentration. The rate of addition is controlled by a peristaltic pump. The isothermal conditions are maintained with a precision of ±0.5 °C and the correction is achieved by increasing or decreasing the rate of gas delivery. It is obligatory to keep a constant rate of stirring for optimal mass exchange. The process is interrupted 45 min after the beginning of CTC addition by introducing hydroquinone and rapidly cooling the reaction system. The product obtained is isolated by precipitation in diethyl ether.

The aim of polymerization in the isothermal regime is to evaluate the influence of CTC mass flow on the final product characteristics.

(ii) Under adiabatic conditions. A mixture of VP in toluene is prepared. It is heated up to 76 °C in the reactor working in an isothermal mode (without cooling water in the reflux condenser). The initiator, dissolved in a small amount of toluene, is added. Ten seconds after that a mixture of CTC in toluene is introduced to the reaction medium with a constant volume flow. The CTC mixture has a relevant concentration and is heated up to 76 °C. In 10 min the reactor is switched on in adiabatic mode—the cooling water, the inert gas, and the circulation of heating fluid are simultaneously stopped. The temperature of the reaction medium is measured after a 10-min polymerization under created adiabatic conditions.

The purpose of carrying out the copolymerization under adiabatic conditions is to study the effect of CTC mass flow on the effective rate of the process. It is known that for this type polymerization the main component of the heat effect is the decrease of molar energy of the bond at the π–σ transition. The frequency of these transitions is simultaneously proportional to the effective polymerization rate and the rate of heat release (the heat power). If the process is carried out under adiabatic conditions and the negligible changes in pressure and volume are ignored, the whole heat of the reaction is needed to increase the temperature of the reaction system. So the rate of temperature increase in the reaction medium is a measure of the effective rate of polymerization under adiabatic conditions.

During the first 10 min of the adiabatic process the graphic increase of temperature as a function of time is approximately a straight line for every one of the conducted experiments. So we can accept that the index of heat power (the effective rate) of the process $\nabla t/\nabla \tau$ (°C/min) is equal to the rate of the temperature increase $\mathrm{d}t/\mathrm{d}\tau$

$$\nabla t/\nabla \tau \approx \mathrm{d}t/\mathrm{d}\tau$$

and it can be calculated by the equation

$$\nabla t/\nabla \tau = 0.1(t_{\mathrm{f}} - t_{\mathrm{i}})\ {}^\circ\mathrm{C/min}$$

where t_{i} is the initial temperature, 76 °C (temperature at the beginning of the adiabatic process), and t_{f} is the temperature at the end of the adiabatic process.

The data obtained at different values of CTC mass flow have to be taken as arbitrary.

Methods of Analysis. The integral composition $\bar{X}$ = VP/MA of the copolymers was established by potentiometric titration.[4] The molecular masses were determined by viscosimetry[6] according to the formula of Mark–Houwink $[\eta] = KM^{\alpha}$, using equal values of K and α for the homopolymer and the

Table I

no.	monomer	soln concn, mol/L	initiator (AIBN), wt %	$t \pm 0.5$, °C	n[a]	$M_\eta \times 10^{-4}$, Da	copolymer comp (VP:MA), mol/mol
1	VP	2.0	0.25	76.0	1080	12	
2	VP	4.0	0.25	76.0	2070	23	
	VP	2.0					
3	MA	2.0	0.25	76.0	81	1.7	1.05:1.0
4	VP	4.0	0.25	76.0	110	2.3	1.08:1.0
	MA	4.0					

[a] Polymerization degree.

copolymers. This approach facilitates the comparison—virtually every copolymer with a viscosimetric molecular weight M_η, calculated on the basis of that of poly(vinylpyrrolidone), constant K, and α, is represented by an imaginary poly(vinylpyrrolidone) with equivalent viscosity as under analysis conditions. In this way it becomes possible to compare polymer products with different amounts of MA, although a systematic error is introduced which increases in value with the increase in MA contents in the product and reaches its maximum in an alternating polymer. The evaluation of the maximum systematic error can be done by comparing the weight-average molecular weight M_w and number-average molecular weight M_n with the calculated M_η'. If the calculation of M_η was carried out with the exact constants K and α for the given copolymer, the following inequality would be valid for the accurate M_η:

$$M_n \le M_\eta \le M_w$$

The values of M_w and M_n are 32 000 and 20 000, respectively, and they restrict the range that the accurate M_η is found. M_η' proved to be 23 000 and consequently

$$M_n < M_\eta' < M_w$$

This means that M_η' and M_η have sufficiently allied values and the maximum error does not exceed 30%.

Samples of poly[(hydroxypropyl)methacrylamide] prepared by IMMC—Prague as standards for investigations with the GPC method were used in determining the MWD of end products.

Results and Discussion

The dominating trend of VP and MA to alternating copolymerization, confirmed by numerous author,[2,4,5] is explained by the independent participation of CTC in the process. CTC is the first included in the composition of the forming copolymer, compared to the rest of the components in expression 1. Therefore, CTC has the greatest affinity toward the growing macroradicals. During the copolymerization process, CTC is exhausted and equilibrium 1 is gradually shifted to the right. In this way the whole quantity of the comonomer, which is in shortage in respect with the other comonomer (VP or MA), can react.

We could not find any satisfactory explanations of the much greater affinity of CTC toward the macroradical in comparison with VP and MA. It is well-known that MA does not homopolymerize and the homopolymerization of VP[7] takes place at high rate and with considerable thermal effect. The reasons for the greater (by several orders of magnitude) affinity of CTC (compared to VP) can be the following: The rate of chain propagation at including CTC is several orders of magnitude higher than that at including VP; i.e., VP apparently manifests zero affinity toward the macroradical, because of the much greater affinity of CTC. The rate of chain propagation at including CTC is commensurable (or considerably lower) than that at including VP. But during every single act of interaction between the macroradical and CTC, VP loses its ability to include in the chain, i.e., during this period of interaction VP really has zero affinity toward the macroradical.

Which of these two variants is predominant? This can be answered if an evaluation of the ratio between the rate of chain propagation for VP homopolymerization and the rate of chain propagation for copolymerization of the VP/MA mixture (molar ratio 1:1), "homopolymerization" of CTC, is made.

Determination of the rate constants of chain propagation is complicated,[7] especially for CTC homopolymerization.

According to the first possibility we have to evaluate the ratio of rates, differing by several orders of magnitude. So, if we accept certain approximations, the average molecular weight of the product, formed during the isothermal homopolymerization of VP and CTC, can be proposed as a measure for the rate of chain propagation. Why? The molecular weight of a polymer is proportional to the kinetical length of the chain (ν).[7] The latter can be presented by the expression

$$\nu = W_p/W_t$$

where W_p is the rate of chain propagation and W_t the rate of chain interrupting, when a polymerization with a π–σ transition take place.

The above mentioned approximation is based on the assumption that if the first supposition (for the greater affinity of CTC) is valid, then W_t should have one and the same value for the two types of homopolymerization (VP and CTC); i.e., ν (or the molecular weight) is a measure of W_p. Consequently, by comparison of the two molecular weights (that of VP homopolymer and the alternating copolymer, obtained under analogous conditions in the isothermal regime), a conclusion can be made for the approximate ratio between the rates of chain propagation of VP homopolymerization and VP/MA alternating copolymerization (the so-called "homopolymerization" of CTC).

Homopolymerization of VP solutions in benzene was performed under isothermal conditions in an inert atmosphere. Analogous "molar" concentrations of CTC in benzene were subjected to homopolymerization under the same conditions. The processes were interrupted after the same amount of time to avoid the gel effect. The solution concentrations the process conditions and the molecular weight of the products obtained are presented in Table I. It is seen that the molecular weight of the alternating copolymer is by more than 1 order of magnitude lower than that of poly(vinylpyrrolidone) obtained under the same conditions; i.e., the rate of chain propagation of CTC "homopolymerization" is considerably lower than that of VP homopolymerization. The data show that a 2-fold decrease of VP concentration in the solution corresponds to a 2-fold decrease of molecular weight, which is in good agreement with the kinetical equation for chain propagation.[7] The 2-fold decrease in the concentration of the VP/MA mixutre (molar ratio 1:1) in the solution decreases the molecular weight of the alternating copolymer 1.4 times only. Therefore, the presented data in

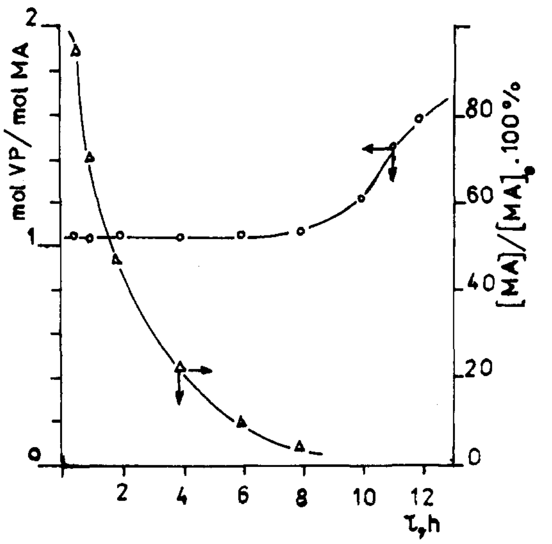


Figure 1. Variation in reaction product composition and MA content during copolymerization of a mixture of VP and MA (2.0:1.0).

Table I give evidence for zero affinity of VP toward the macroradical when there is MA in the reaction medium.

Under the same conditions (Table I), copolymerization of a mixture of VP and MA (molar ratio 2:1) in benzene was carried out. Samples were withdrawn from the reaction medium at equal time intervals and the copolymer formed was isolated by precipitation in a controlled volume of ether. The composition of the copolymer and the MA content in the reaction medium were determined; the results are plotted in Figure 1. Figure 1 depicts the correlation that exists between the period of dominating tendency toward alternation and the period of MA consuming because of the copolymerization. It is clearly seen that this tendency is interrupted at the moment when there is a complete consumption of MA in the reaction system, i.e., only then the homopolymerization of VP begins. Or, in other words, only when MA is completely consumed is the ability of VP to homopolymerize "recreated".

The data from Table I and Figure 1 allow us to draw a conclusion: during every single act of interaction of CTC with the growing macromolecule, the affinity of VP toward the macroradical is zero, independent of the act duration. Obviously, the incorporation of CTC covalently into the macroradical is not a single-act process. The process is as follows: (a) first act—much faster than the act of VP homopolymerization, when CTC blocks the macroradical and prevents it from interaction with VP; (b) final act—considerably slower then the act of homopolymerization, when CTC covalently is involved in the growing macroradical. The question arises, is it possible for the fast act of interaction between the macroradical and CTC to take place with a rate commensurable with the homopolymerization of VP, if the concentration of MA (respectively CTC) in the reaction system is sufficiently reduced?

In order to answer this question, studies on the described model of interaction in adiabatic and isothermal regimes were carried out. The correlation of data obtained was examined, too. The process parameters, the concentration of the solutions used, and the data obtained are given in Table II.

The data from Table II confirm the conclusion for the non-one-act incorporation of CTC into the growing macroradical. There is an apparent anomaly: the thermodynamic estimation of the process and the stoichiometric estimation of the final products have given just the opposite results. From a thermodynamical viewpoint, it is VP that sums to be more active during polymerization, whereas on the basis of stoichiometric data CTC is incorporated into the final product to a higher extent (MA always reacts to almost 100%).

The heat power of the adiabatic polymerization is presented by the expression $\nabla t/\nabla \tau$ (C/min)—the average rate of temperature increase. Under the conditions of our interaction model the heat power is a sum of two components: heat power of CTC polymerization; heat power of VP polymerization.

The data in Table II show that the heat power is not considerably changed until one fixed limit value of mass flow decrease and, under the same conditions and same decrease of CTC mass flow in isothermal regime, a copolymer with uniform composition VP:MA = 1:1 (molar ratio) is formed. In other words, as the mass flow decreases until that threshold there is a practically unchanging effective rate of polymerization and a constant composition of the copolymer formed (1:1) with both polymers having the same molecular weight. It is evident that until that threshold of mass flow decrease, the copolymerization is wholly alternating and the second component of the heat power (VP polymerization acts) is zero.

The decrease of CTC mass flow below that limit leads to a clearly expressed increase of the heat power of the process; i.e., the effective rate the copolymerization enhances. Obviously, the second component of the heat power is as much bigger than zero as the value of the mass flow in this range of CTC mass flow values is smaller. The copolymerization data show that the rate frequency of effective rate increase (when the mass flow decrease) is equal to the rate frequency of increasing the relative part of VP units in the composition of the corresponding copolymer and its molecular weight (this is expected, taking into account the data from Table I).

When the mixture of VP and MA (mole ratio 1:1) is introduced to the reaction system with a definite mass flow, a relevant concentration of CTC is created. From this the following conclusions can be reached: CTC both simultaneously suppresses the homopolymerization activity of VP and is involved in the formed copolymer. If the CTC concentration in the reaction medium decreases, it is observed that until a limit value blocking of the homopolymerization activity of VP is complete and below that limit value it is partial. The extend of deblocking of VP homopolymerization increases with the decrease of CTC concentration and corresponds to an increase in the relative part of VP units in the formed copolymer with the same rate frequency.

The blocking (inhibition) of VP homopolymerization and the covalent incorporation of CTC in the composition of the end product, considered as an integrated act of polymerization, show that there are at least two consecutive acts in this complex process: the act of inhibition (blocking) is much faster than the homopolymerization act of VP (Figure 1); the act of CTC covalent incorporation in the polymer chain has a rate considerably lower than that of VP homopolymerization (Table II—studies in the adiabatic regime).

The existence of a limit that separates the CTC concentration range into "alternating" and "nonalternating" shows that at this limit the factor that limits the rate of VP homopolymerization inhibition is changed. Obviously, within the "alternating" limits, the rate of inhibition is in the kinetic region (defined directly by the driving force of the process). Within the "nonalternating" limits this rate is in the diffusional region (defined by the rate

Table II

no.	CTC soln, mol/L		added amt × 10^9, mol/min	VP soln, mol/L	AIBN × 10^2, mol/L	adiabatic regime		isothermal regime		
	VP	MA				t_f, °C	$\nabla t/\nabla \tau$, °C/min	$M_\eta \times 10^{-4}$, Da	X = VP/MA, mol/mol	reacted MA, wt %
1	5.5	5.5	7.15	4.0	1.22	79.2	0.32	1.8	1.5:1.0	98.0
2	5.0	5.0	6.50	4.0	1.22	79.2	0.32	1.7	1.5:1.0	99.0
3	2.5	2.5	3.25	4.0	1.22	79.9	0.39	2.3	2.8:1.0	97.0
4	1.0	1.0	1.30	4.0	1.22	80.7	0.47	3.9	3.8:1.0	97.0
5	0.5	0.5	0.65	4.0	1.22	83.0	0.70	6.5	6.8:1.0	97.0

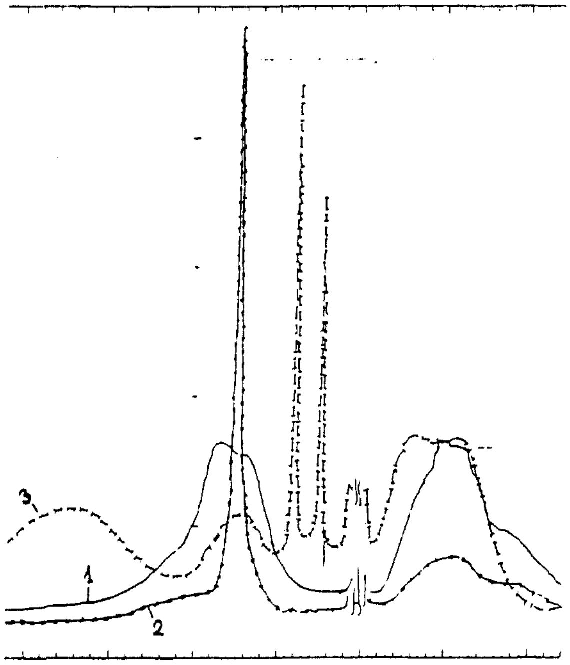


Figure 2. Results from an investigation by NMR of a copolymer of VP and MA with X = 6:1 (1), poly(vinylpyrrolidone) (2), and alternating copolymer (3).

of diffusion of the active particles toward the interaction field). The stationary concentration of CTC rises in the "nonalternating" range when there is a sufficiently effective agitation. The value of the stationary concentration depends on the value of mass flow of the VP/MA mixture (1:1). Therefore, the mass flow by the stationary concentration of CTC affects the effective rate of polymerization and this influence is commensurable with the rate efficiency with which it affects the VP content and molecular weight in the obtained copolymer. In other words, the dynamics of the polymerization process and the characteristics of the end product can be regulated by the CTC mass flow. This conclusion offers the possibility for synthesis of VP/MA copolymers with a kinetically regulated structure of the macromolecule. This type of synthesis can be realized after creating a reverse link, necessary for the stability of regulation. So the reverse link is a mechanism for an adequate decrease of VP/MA mass flow at which the hold CTC concentration follows the VP consumption in such way that their ratio always remains constant with the time.

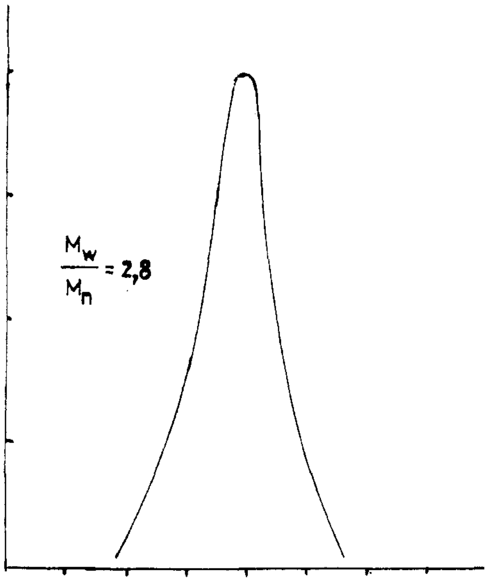


Figure 3. Differential curve of the molecular weight distribution of the VP/MA copolymer (molar ratio VP:MA = 6.5:1.0).

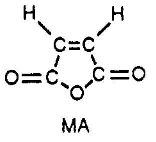
Figure 2 presents the results from analysis of the copolymer with VP/MA = 6.5:1.0 by the NMR method in dimethyl sulfoxide. The spectrum is compared to the corresponding spectra of an alternating copolymer of VP and MA and poly(vinylpyrrolidone). It can be seen that the double narrow resonance band characteristic for the alternating sequence of MA units in the macromolecule of the alternating copolymer is not observed in the statistic copolymer spectrum. The resonance bands characteristic of the homopolymer are broadened and have a quite different height ratio in the case of the statistic copolymer. These differences are due to the influence of the acceptor MA units on the donor VP units.

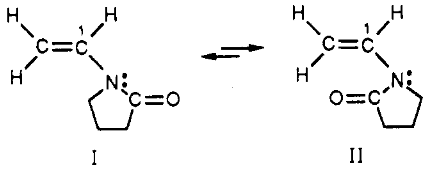
The effective agitation of the reaction medium is a very important circumstance for correctness of the data obtained. A certain information about an effective agitation can be received from Figure 2—the lack of alternating sequences excludes the presence of local heterogeneities in the agitated system. A criterion for effective agitation is the molecular wight distribution for the copolymer. Ineffective agitation leads to the above-mentioned heterogeneities (local) in the volume of the reaction medium—some of them enriched with VP, others with CTC (compared to the average concentration values of the system). It is seen from Table II that the ratio of VP and CTC concentrations significantly affects the molecular weight of the end product. The presence of local heterogeneities would lead to a broad molecular weight distribution. Figure 3 gives the differential curve of the molecular weight distribution of a statistically formed polymer (VP:MA = 6.5:1.0). The ratio M_w/M_n is equal to 2.8. The data plotted in Figure 3 show that the parallel reacting of VP and CTC under created conditions is not a result of the poor mass transfer in the reactor due ineffective agitation.

The experimental data confirm the conclusion of the above cited authors for the dominating tendency toward alternation during the copolymerization of VP and MA. Analyzing the results, given in Table II, it becomes clear that the inhibition of VP homopolymerization is caused by loss of activity of the macroradical with an active end VP unit ($M^{\bullet}_{vp}$) with respect to the free VP. This lowering of the macroradical activity could be due to MA action—direct or indirect. Such an effect MA can provoke alone or in the form of CTC. This is well seen from the components of the equilibrium system (1). MA or CTC, as a result of the polar interaction with the active end of macroradical ($M^{\bullet}_{vp}$), forms an intermediate complex. The disintegration of the intermediate complex leads to incorporation of one MA unit covalently into the growing macromolecular chain. The macroradical ($M^{\bullet}_{ma}$) thus obtained has decreased activity because of clearly expressed resonance stability and it is able to react only with the VP molecule.

When commensurable amounts of VP and MA react it is difficult to determine if the growing macroradical $M^{\bullet}_{vp}$ forms a complex with MA or CTC. For the accepted experimental model of copolymerization an alternating copolymer is formed even when the VP concentration is several orders of magnitude higher than that of MA (Table II, the first two examples). If we accept that the equilibrium constant[1] of CTC is on the order of 10^{-1}, it can be easily estimated that for the examples given Table II MA practically is completely in the form of CTC. If MA directly forms an intermediate complex with $M^{\bullet}_{vp}$ under the conditions of infinitely low MA concentration, the rate of complexing could be only in the diffusion region; i.e., a nonalternating copolymer had to form. But the fact is that an alternating copolymer is formed and this shows that the second alternative is valid—an intermediate complex if formed during the interaction between $M^{\bullet}_{vp}$ and CTC.

From the experimental data the most probable individual acts, leading to the formation of an intermediate complex, can by considered. First, it is necessary to accentuate on some MA and VP peculiarities:


MA


I

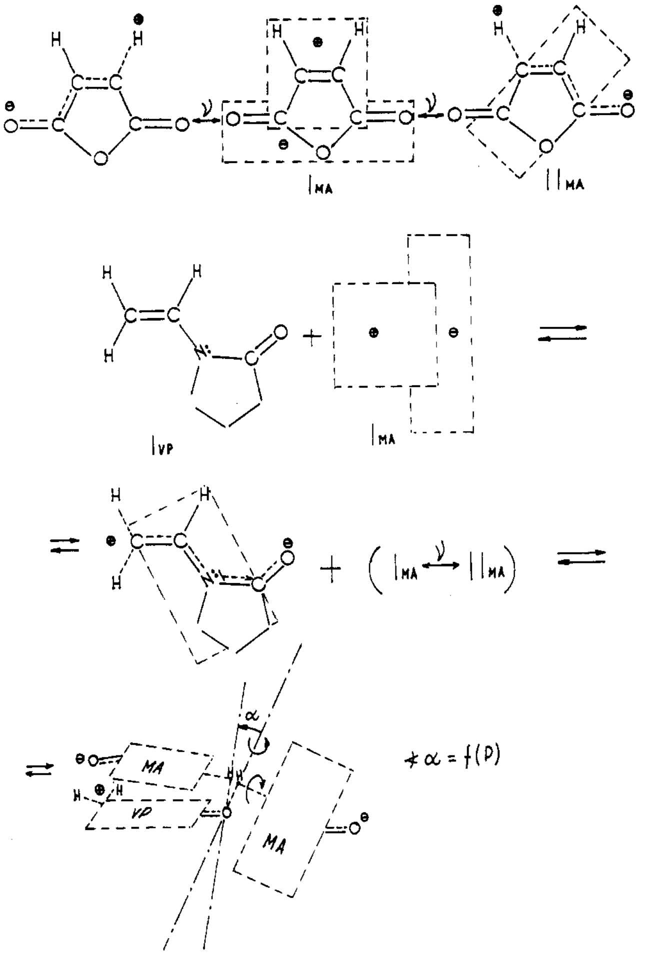
II

VP

The molecule of MA is a coplanar dipole. It possesses a conjugated system of mobile electrons. The system of mobile electrons is tense because the two negative induction effects with opposite directions are balanced on it. The C–H bonds are partially polarized, too. In other words, MA represents a planar dipole with a high dipole moment but with distributed charges and with a small distance between them (a short dipole arm). When a donor/acceptor interaction takes place, the polarization of the C–H bond goes deeper and the stress equilibrium of the conjugated system of electrons is broken. This is done by electron transfer toward the donor, which provokes an effective transfer of negative charge in the MA chain of conjugation. CTC is formed, for which the dipole arm is significantly longer and the charges much more localized in comparison to MA.

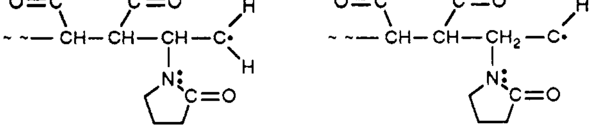
The molecule of VP is a combination of two planar structures—that of the vinyl group and that of the pyrrolidone ring. The C^1–N bond lies simultaneously in the two planes. As a result of rotation around the C^1–N bond, two coplanar conformers can be formed, placed at an angle π—I and II. For these two conformers the π-electrons of the vinyl bond are conjugated with the p–π system of the amide group. Because of that only the coplanar conformers have significantly dipole moments and clearly expressed donor properties. The rotation around the C^1–N bond is complicated due to the influence of the negative induction effect on the conjugated electron system in the conformers. So the complanar conformers are the most probable condition of the VP molecule.

Scheme I



The donor–acceptor complex (CTC) is formed as a result of the polar interaction of MA with the VP coplanar conformer (probably the two conformers have this complexing ability). A complementary dipole moment is induced in the VP molecule and the stress equilibrium is broken in the MA molecule (Scheme I). Opposite charges are localized in the donor and acceptor because of proton transfer from MA toward VP and an effective transfer of negative charge along the chain of conjugation in the MA molecule. A coordination of the two planar molecules takes place, under the influence of proton transfer and the probably polar interaction of the localized charges with one another. The planes of MA and VP molecules most probably are coordinated at a certain solid angle smaller than $\pi/2$ and by force accumulate some configurational stress. A decrease in the intensity of the characteristic for the CTC green color as the polarity of the solvent increases is indicative of that coordination.

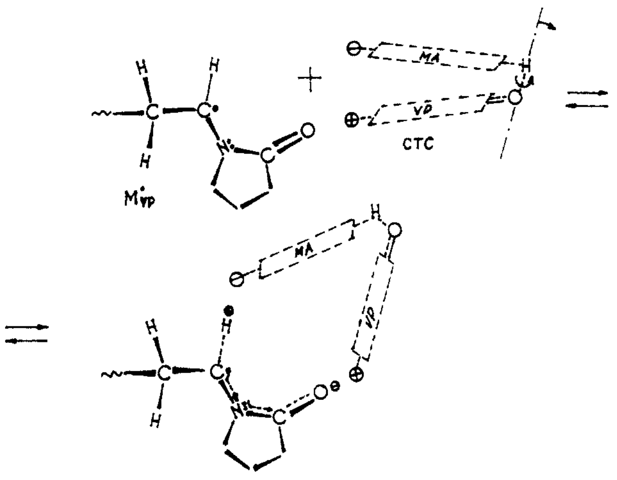
The VP unit is attached by two different combinations to the active end of the macroradical $M^{\bullet}_{vp}$: III, tail-to-head arrangement; IV, head-to-tail arrangement. In the first case (III) the dipole moment of the unit is very small, while in the second case (IV) the uncoupled electron of


III

IV

$M^{\bullet}_{VP}$

Scheme II



$M^{\bullet}_{vp}$, conjugated with the p–π system of the amide bond, makes it significant. When there is an external polar action an additional dipole moment is induced. Most probably, this dipole enters the space between localized charges of CTC during the interaction of $M^{\bullet}_{vp}$ with CTC.

If we accept the above-described CTC coordination, then the dipole entering (the dipole of the active end of $M^{\bullet}_{vp}$) leads to enlarging the solid angle between MA and VP, i.e., to lowering the configurational stress in the CTC molecule. That is the reason for the relative stability of the formed intermediate complex. Figuratively speaking, CTC "takes the active end of $M^{\bullet}_{vp}$ in its teeth" and sterically screens in from VP (Scheme II).

The chain of charge transfer becomes longer compared to CTC in the intermediate complex. In this charge transfer the uncoupled electron of $M^{\bullet}_{vp}$ takes part, too, and this makes the macroradical resonance stabilized; i.e., it has lowered activity toward VP. Consequently there are two the probable reasons for homopolymerization activity loss of VP: a steric screening of the active end of $M^{\bullet}_{vp}$ because of coordination with CTC; participation of the uncoupled electron of $M^{\bullet}_{vp}$ in the charge transfer of the intermediate complex.

The disintegration of the intermediate complex most probably is done at a certain critical level of isothermal accumulation of energy. When this disintegration takes place the molecule of MA turns out to be sufficiently close to the active end of $M^{\bullet}_{vp}$. So there is a real chance a covalent attachment to be realized. The free MA also realizes a polar interaction with $M^{\bullet}_{vp}$, but because of its small dipole arm, distributed charges, and the steric effect of 1,2 substitution of double bond, it cannot come near $M^{\bullet}_{vp}$—near enough to assure a covalent incorporation.

The macroradical with one unit of MA ($M^{\bullet}_{MA}$) as the active end is resonance stabilized. So the covalent incorporation of VP (MA does not react) into $M^{\bullet}_{MA}$ has a very slow rate—probably it is the slowest step of CTC incorporation into the chain.

When the concentration of CTC is in the "alternating" range, $M^{\bullet}_{vp}$, immediately after its formation, inevitably realizes a polar interaction with CTC and becomes inaccessible to VP. When the CTC concentration is in the "nonalternating" range, in order to be able to react with $M^{\bullet}_{vp}$ CTC has to go through diffusion passage. It should be noted that during the time from its formation till its polar interaction, the macroradical is normally active with respect to VP. The number of VP units that can be incorporated into the chain during this period depends on the ratio

$$W_{vp}/W_d \qquad (2)$$

where W_{vp} is the rate of chain propagation in return for VP homopolymerization and W_d is the rate of CTC diffusion.

Obviously, the molecule of the copolymer obtained has long sequences of VP units alternating with single MA units. The NMR analysis (Figure 2) and the results of copolymerization studies in adiabatic regime confirm without doubt the suggestions made, which try to clarify the most probable individual act of interaction.

Conclusion

1. Independent of how low the content of MA in the comonomer mixture with VP is the tendency toward alternation is preserved. There is a minimum value of MA concentration up to which an alternating copolymer is obtained. When MA concentration is below that value, a copolymer characterized with long sequences of VP units alternating with single MA units in the macromolecule is formed.
2. The most active component of the comonomer mixture is CTC, formed from VP and MA. It has a very high rate of polar interaction with the growing macroradical, which has VP as its active end. This interaction blocks the homopolymerization activity of VP and causes covalent incorporation of MA into the growing macrochain.
3. The rate of propagation of the copolymer chain in return for the covalent incorporation of CTC components is lower compared to the rate of propagation in return for the homopolymerization of VP.
4. The rapid coordination of CTC with the macroradical in combination with its relatively slow covalent incorporation into the growing chain allows regulation of the effective rate of copolymerization by maintaining a sufficiently low MA concentration in the system. Thus, this is the way to synthesize copolymers with a kinetically regulated structure of the macromolecule.

References and Notes

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Registry No. VP/MA (copolymer), 26837-56-9; VP/MA (alternating copolymer), 106102-95-8.