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MECHANOCHEMICAL POLYMERIZATION OF METHACRYLAMIDE IN THE SOLID STATE

For initiating the polymerization of monomers in the solid state, recently, along with radiation methods, chemical[^1] and even mechanical[^2] methods of action have been used increasingly often. In the latter case it was shown that intense mechanical action on crystals of salts of acrylic acid causes their polymerization in the absence of any additional sources of initiation, owing to the formation of active centers of the electron-donor type in the lattice of ionic crystals. Continuing studies in the field of polymerization of monomers on freshly formed surfaces of inorganic substances[^3], we found that

[Figure 1 and Figure 2 graphs]

Fig. 1. Dependence of the yield of polymethacrylamide on the duration of dispersion in the presence of 0.5% NaCl

Fig. 2. Dependence of the yield of polymethacrylamide on the concentration of catalyst:
a –NaCl–MAA; *b* –$BaSO_4$–MAA; *c* –NaCl–MAA–heptane

intense mechanical dispersion of such compounds as NaCl, $BaSO_4$, or SiO_2 in a monomer medium causes polymerization not only of monomers in the liquid state, but also of solid crystalline monomers. The present communication describes the mechanochemical polymerization of solid methacrylamide.

Commercial methacrylamide (MAA) was subjected to threefold recrystallization from benzene, m.p. 104°. As polymerization catalysts we used common salt, barium sulfate, and quartz sand, which were purified and dried according to classical procedures. A weighed portion of monomer and catalyst (total weight 5 g in all experiments) was placed in steel drums filled with steel balls and subjected to vibrational action in a laboratory eccentric vibratory mill in accordance with the procedure described earlier[^4]. The reaction products were separated by fractional precipitation with methanol from aqueous solutions and by selective extraction with benzene.

Figure 1 shows the dependence of the yield of polymethacrylamide (PMAA) on the time of dispersion in the presence of 0.5% NaCl at room temperature. After a short induction period, the rate of polymeriza-

Fig. 3. Degree of conversion of MAA as a function of the concentration of SiO_2 (a) and NaCl (b). I —polymer, II —oligomers

Figure 1: Fig. 3. Degree of conversion of MAA as a function of the concentration of SiO_2 (a) and NaCl (b). I —polymer, II —oligomers

tion first increases, and then decreases, and the amount of polymer formed remains constant. The kinetic curve has the same form as in the case of polymerization of liquid styrene in the presence of SiO_2 ([4]) and liquid acrylonitrile in the presence of Fe ([5]) during vibrational dispersion of these systems under analogous conditions.

Fig. 3. Degree of conversion of MAA as a function of the concentration of SiO_2 (a) and NaCl (b). I —polymer, II —oligomers

A change in the monomer-catalyst ratio has a strong effect on the efficiency of polymerization. Fig. 2 gives the dependence of the amount of polymer formed on the NaCl-MAA and $BaSO_4$-MAA ratios during 45-minute dispersion at 20°. It is seen from Fig. 2 that polymerization already occurs when the NaCl content in the system is 0.005%, and at 0.5% the degree of conversion is maximal (10%). With a further increase in the amount of NaCl in the system, the polymer yield decreases and at 80-90% salt falls to zero. Exactly the same dependence is also observed for the $BaSO_4$-MAA system (Fig. 2). In the case of crystalline quartz, the process is similar in character (Fig. 3a), but with a sharper maximum at 5% SiO_2 content in the system.

The decrease in the yield of polymethacrylamide at high catalyst contents, as it turned out, is not connected with an overall decrease in the degree of conversion of MAA, which would be strange, but is connected with a decrease in the content of the high-molecular PMAA fraction in the reaction products and an increase in the amount of oligomers. Cryoscopic determination of the molecular weight showed that dimers or trimers of MAA are formed. Fig. 3b shows the yield of oligomers (the sum of dimers and trimers) as a function of the NaCl content in the system. A similar phenomenon also occurs in the case of the SiO_2-MAA system (Fig. 3a). It is characteristic of both systems that, at the maximum yield of high-molecular PMAA, the amount of oligomers formed is extremely small, and it increases only as the yield of the former decreases.

Table 1

	0.5	5	10	20
NaCl content in mixture with MAA, %	0.5	5	10	20

	0.5	5	10	20
[η] of the high-molecular fraction—PMAA[1]	0.145	0.148	0.150	0.150
Mol. wt. of oligomeric fraction	255.8[2]	244.2[2]	171.6[3]	168.4[3]

[1] Determined in aqueous solutions at 18°. [2] Mol. wt. of MAA trimer 255. [3] Mol. wt. of MAA dimer 170.

Table 1 gives the results of measuring the viscosity of the high-molecular PMAA fraction and data on the cryoscopic molecular weights of the oligomers at different NaCl ratios in the polymerizing system at room temperature. From the data in Table 1 it follows that the products

products of MAA polymerization at all ratios of monomer and catalyst are a polymer with an intrinsic viscosity of 0.15, trimers and dimers of MAA. This fact, curious in itself, still requires special study; however, the preliminary data suggest that the processes of polymerization and oligomerization are independent reactions proceeding in parallel. To elucidate the role of the phase state of MAA in mechanochemical polymerization, special experiments were carried out on the dispersion of NaCl, $BaSO_4$ and SiO_2 in the presence of molten monomer at 120° (the indicated compounds are insoluble in the melt), and also in the medium of aqueous (with additions of $BaSO_4$ and SiO_2) and benzene (with additions of NaCl and $BaSO_4$) solutions of MAA at 20°. In none of these cases was polymer formation observed. At the same time, introduction into the NaCl—MAA system of an inert liquid—heptane—has absolutely no effect on the effectiveness of polymerization (Fig. 2). These results indicate the role of the solid state of this monomer as a necessary condition for the occurrence of the mechanochemically initiated polymerization process.

It may be assumed that the mechanism of initiation of polymerization in the NaCl—MAA and $BaSO_4$—MAA systems is analogous to that proposed by us earlier for the systems ionic salt—vinyl monomer ([2],[5]), involving the formation of an ion-radical through the addition of an electron to the monomer molecule, which is highly prone to radical polymerization. The sources of electrons are defects of the F-center type, arising in the lattice of ionic salts under the action of mechanical forces and ionizing with emission of electrons. The suppression of MAA polymerization with 0.5% NaCl and 0.5% hydroquinone under analogous conditions (the yield of PMAA is 0.34% after 45 min of dispersion) indicates the radical character of the polymerization. In the case of SiO_2, as has been considered in detail in a number of works ([3]-[5]), mechanical grinding leads to the

formation of centers of the radical type through rupture of the covalent bonds Si–O–Si.

The distinctive feature of initiation under the present conditions, in comparison with the systems described, is that this stage of macromolecule formation must include transfer of the active center from one solid phase to another, from the salt or quartz to solid methacrylamide. In this case, the affinity of these phases for one another and their mutual wettability play a major role. It is possible that the absence of polymerization of styrene and methyl methacrylate when they are dispersed in the frozen state in the presence of the solid salts NaCl and $BaSO_4$ is connected precisely with the poor wettability of these two solid phases, whereas the same monomers polymerize under analogous conditions when in the liquid state. Methacrylamide, as a molecular crystal of a more polar character than styrene, has greater affinity for ionic salts.

We have repeatedly ascertained that the polymerization of MAA in the presence of salts proceeds quite effectively not only at room temperature but also at considerably lower temperatures, down to −150°, i.e., 250° below the melting point of the monomer. (In the latter case the experiments were carried out in drums cooled with liquid nitrogen according to the method described in ([6]), or in glass ampoules ([5]).) Since neither in solution nor in the melt of MAA does polymerization occur under the conditions studied, attention is drawn to the fact of high polymerization rates far from the melting temperature and in the absence of phase transitions necessary for the realization of a definite mobility of monomer molecules, ensuring rapid growth of polymer chains ([7]). Indeed, it has already been pointed out ([7]) that polymerization reactions in the solid phase can proceed at high rates only if the ordering of the monomer molecules is combined with their definite mobility, owing to the inhibiting influence on chain growth of defects in the crystal lattice of the monomer that inevitably arise during the reaction. Phase transitions in the solid monomer, provided there exist accum–

···of active centers prepared in advance is one of the possibilities for the rapid healing of defects. It should be assumed that, during continuous mechanical crushing of the monomer crystals, the freedom of displacement of molecules on the surface of solid particles is very close to their mobility at the moment of a phase transformation. Thus, in the system under study, conditions are created for the occurrence of rapid, nonactivation growth of polymer chains (a monomer conversion of 10 and 40% in 45 min should unquestionably be regarded as a rapid polymerization process, if compared with the rates of radiation polymerization of crystalline monomers, in particular acrylamide and methacrylamide [8], which continues for months).

If the ideas set forth above are correct, then, at equal efficiency of grinding of the monomer crystals in a given mixture with catalyst, the polymerization rate within the solid state should not depend on temperature at a constant initiation rate. Indeed, the formation of 6% PMAA at −150° (10% PMAA at +20°) shows that, when the temperature is changed by 170°, the polymer yield decreased only

by a factor of 1.6. An approximate estimate of the activation energy of MAA polymerization in this case gives a value on the order of 0.1 kcal/mole, which means practically zero activation work.

With continuous renewal of the surface of the solid monomer, new defects are constantly formed and old ones are healed; this, with the simultaneous ongoing process of generation of active centers, creates conditions for the rapid development of the polymerization chain in an ordered system. Thus, in the present case the most reactive entity is the most defective crystal lattice of the monomer, and not the ideal crystal. Let us note that chain termination also occurs at defects, and not through recombination of radicals, since the molecular weight of PMAA obtained at -150° is almost no different ($[\eta] = 0.17$) from the molecular weight of PMAA obtained at $+20^\circ$ ($[\eta] = 0.15$), i.e., it is associated with identical conditions for the development of the polymerization process under mechanochemical action, irrespective of temperature.

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Note: Figure translations are in progress. See original paper for figures.