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Investigation of acrylonitrile polymerization on the surface of porous microspherical silica gel

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Abstract

The kinetics of acrylonitrile polymerization on the surface of porous microspherical silica gel (PMSS) was studied and some kinetic parameters were determined. The structure of PMSS-based sorbents was analyzed by FTIR-spectroscopy, XRD and sorption analysis before and after microcapsulation with polyacrylonitrile.

Keywords: Silica gel; Acrylonitrile; Polymerization

1. Introduction

New methods of synthesizing and characterizing chromatographic composite sorbents, are needed for both fundamental and applied research. In addition, polymerization on the surface of colloidal composite fillers improves filler uniformity because polymerizing monomer fills open pores and cracks; in addition, the degree of hydrophobicity of fillers increases [1–3]. Surface polymerization is applicable to other materials (ion exchange membranes, polymer fillers, chromatographic sorbents) where a protective polymer coating or encapsulation of a solid is required [4].

The aim of the present work is to determine the kinetic parameters and to analyze the structural changes of resulting sorbents after microencapsulation of PMSS silica with polyacrylonitrile (PAN).

2. Experimental section

2.1. Materials

Acrilonitrile (AN) (‘Navoiazot’ Co., Uzbekistan) was purification with 5% aqueous solution of caustic potash, then dried over calcined calcium chloride and distilled. Porous microspherical silica gel (PMSS) was prepared as described in [5]. The particle size was 3–10 μm. Potassium persulphate and sodium metabisulphite (Angarsk Chemical Co., Russia) was recrystallizated from ethanol.

2.2. Synthesis

PMSS (10 g) was mixed with 150 g of distilled water and 11 g of acrylonitrile and stirred for 10 min and then heated at 40 °C under nitrogen atmosphere. Potassium persulphate (0.15 g) and 0.075 g of sodium metabisulphite dissolved in 10 g of water was added drop wise into mixture of PMSS with AN and stirred for 3 h. The encapsulated product was filtered off, washed in water and dried at 60 °C.

2.3. Characterization

XRD analysis of the samples was performed on a Dron-3M diffractometer with monochromatized Cu K_α radiation at a voltage of 15–30 kV and a current of 15–20 mA, which were adjusted for each sample. Diffraction patterns were recorded at angles of $2\theta = 10–25°$. The samples were prepared by pressing the ground preparations into tablets.

FTIR spectra of the samples were recorded on a Specord-75 IR spectrometer in the 400–4000 cm^{-1} range. The tablets were prepared by pressing the ground preparations along with KBr.

The sorption properties of the initial and PAN-modified PMSS samples were analyzed on a high-vacuum sorption

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apparatus equipped with a mercury seal and a McBain quartz balance. Measurements were conducted with a KM-8 cathetometer (Izyumovskiy instrumental factory, Russia) at the residual pressure of 10^{-3} Pa and 25 °C. Water and benzene were used as sorbates.

The principle of cathetometers work is based on comparison of the measured length (distance between two points of object) from millimetre a scale of the device by sighting (vising) of visual tube on the beginning and the end of the measured piece (segment).

3. Results and discussion

The adsorption of vinyl monomers on the surface of solid can occur by forming ‘strong’ or ‘weak’ bond with adsorbed molecules. AN adsorbed on silica represents a system with a weak bond. Such systems are characterized by the fast reaction rates and are, therefore, of practical interest. In these weak bonds non-specific adsorption takes place, which is reversible near room temperatures.

The influence of initiator concentration on the rate and yield of polymer was investigated at varying the concentration of initiator [$NaHSO_3+K_2S_2O_8$] from 3.46×10^{-3} to 9.46×10^{-3} mol/L. It was shown that the yield of polymer increased with initiator concentration.

The kinetic order of the reaction by the initiator (n), 0.57, was found from the logarithmic curve of the rate of polymerization as a function of the concentration of initiator (Fig. 1). It is known that termination of kinetic chains by quadratic mechanism prevails for AN polymerization on the silica gel surface [6]. The change in n from its usual value of 0.5 could be attributed to the increasing of possibility of kinetic chain termination by linear mechanism, using OH-groups of the silica gel surface. Possible that these groups could be as essential agents of kinetic chain termination [6, 7]. In this case the termination at the kinetic chains could lead to formation of $\equiv Si\cdot$ or $\equiv SiO\cdot$ radicals. The formed radicals had less activity in the reaction propagation compared to macroradicales of the growing chains and kinetically its behavior evinced as the termination of the kinetic chains.

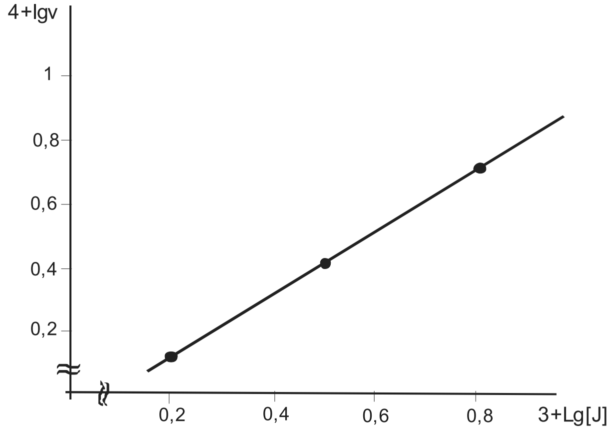

Fig. 1. Logarithmic dependence of the process rate on the initiator concentration.

Since AN was partly dissolved in water, the existence of two-phase liquid system was possible resulting in heterophase polymerization. In this case the concentration of monomer would be more in one of the phase whereas in other it would be significantly less. The regions of polymerization could describe as follows:

1. Polymerization in solution—aqueous-phase polymerization, which depends on concentration of free monomer and the rate of polymerization, is similar that in organic solvents if the concentrations of the monomer and catalyst are comparable. The molecular weight of the resulting polymer is similar to that obtained in organic solvents [8,9].
2. Surface polymerization—surface polymerization depends strongly on amount of adsorbed monomer. The rate of surface polymerization must be higher than the rate of polymerization in solution.

The influence of temperature on the polymerization of AN on silica gel surface was studied at the various of temperature from 40 to 60 °C. The obtained results showed that the yield of polymer on the silica gel surface decreased with increasing temperature (Table 1), possible due to a decrease of monomer concentration in sorption layer on surface of silica gel at increasing temperature.

The effect of monomer (AN) concentration on the polymerization rate was studied at different monomer concentrations in the initial mixture (0.40, 0.59 and 1.13 mol/L). It was shown that the yield of polymer increased with AN concentration. The kinetic order of reaction be monomer concentration (m) was calculated from the logarithmic curve of the rate of polymerization as a function of the monomer concentration and its value was $m=1.2$. The obtained results allowed to assume that the dominant stabilization of active centers formed in the initiation process occurred on the surface silica gel particles.

The polymerization of AN was carried out at AN/silica ratios of 1/1.8, 1/2.4, and 1/3.6 wt%. The value of the rate process and yield of polymer significantly increase with content silica gel. Probably stabilization of growing radicals

Table 1
Influence of temperature on the polymer yield ([$NaHSO_3+K_2S_2O_8$]$=6.46\times10^{-3}$ mol/L; monomer/silica gel = 1:2.4 wt%; [AN] = 1.13 mol/L)

Time (min)	Yield (%)		
	40 °C	50 °C	60 °C
15	4	2	1
30	6	4	2
60	9	6	4
90	15	9	6
120	21	13	7
180	41	25	10

on the silica gel surface which leaded to decrease of the rate of the termination reaction [10] as well catalytic effect of surface on the disintegration of initiator and orientation AN molecules on the surface of silica gel even if there were not active centers was reason of such type behavior of the investigated systems. For all systems studied the following trends are observed: the rate decreases initially, but eventually increases at larger conversion (Table 2). We also analyzed the structure of PMSS sorbents before and after modification with PAN at various ratios. XRD analysis shows that, even at PAN:PMSS = 1:1, the modified polymer show up as a small peak near $2\theta = 17°$ rather than as a strong maximum typical of PAN (Fig. 2) This difference suggests that strong hydrogen bonds are formed between PMSS and PAN due to orientation of the dipolar PAN units with their negative pole toward the surface silanol groups.

The breadth of the FTIR spectra of the initial and PAN-modified PMSS samples implies that the structure of the sorbent is amorphous. FTIR spectroscopy cannot provide detailed information on the interaction of PAN molecules with PMSS surface because the spectra of these compounds overlap in certain regions. Silica gel shows absorption bands of hydroxyl groups belonging both to water molecules and silica gel as well as bands attributed to hydrogen bonds between them. In the spectral range below 1200 cm^{-1}, modes of the silica gel skeleton and adsorbed water molecules bending vibrations are located. The strong absorption band in the 950–1200 cm^{-1} range belongs to Si–O stretching modes. Weaker absorption bands belonging to overtones and combined vibrations of the silica gel framework are located in the 800–2000 cm^{-1} range where they overlap with the bending mode of adsorbed water. A spectral window free of the silica gel and water bands, which can be used record the spectra of organic compounds, is located within 2000–3000 cm^{-1}. The stretching mode of C≡N group (ν_{CN}) at 2245 cm^{-1} falls into this window (Fig. 3).

Table 2
Influence of polymerization conditions on the process rate and yield ([$NaHSO_3 + K_2S_2O_8$] = 6.46×10^{-3} mol/L; monomer/silica gel = 1/2.4 wt%; $T = 40$ °C)

Time (min)	Yield (%)	Rate of process, 10^{-3} V (mol/L s)
[AN] = 1.13 mol/L		
15	4	0.676
30	6	0.507
60	9	0.380
90	15	0.422
120	21	0.443
180	41	0.577
[AN] = 0.59 mol/L		
15	2	0.338
30	4	0.338
60	7	0.296
90	10	0.282
120	14	0.296
180	24	0.338
[AN] = 0.40 mol/L		
15	0.8	0.135
30	1.5	0.127
60	5	0.211
90	7	0.197
120	10	0.211
180	18	0.253

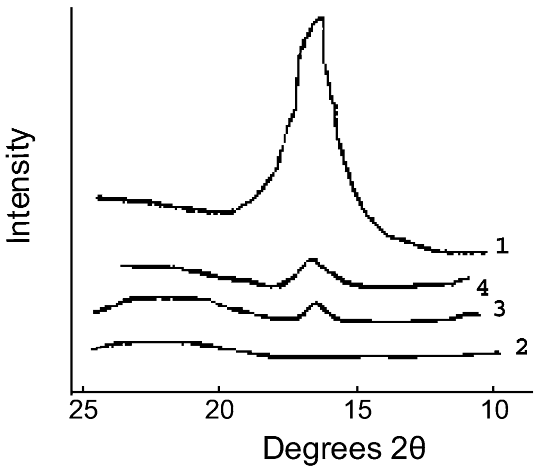

Fig. 2. XRD patterns of (1) PAN, (2) initial PMSS, (3) PAN-modified PMSS, and (4) PAN–PMSS (1:1) mechanic blend.

The continuous absorption in the 3000–3700 cm^{-1} range corresponds to the fundamental stretching silanol groups and water. The observation that the weak adsorption band at 3750 cm^{-1} (belonging to silanol groups free of hydrogen bonding) disappears after modification suggests that silanol interacts with acrylonitrile.

The sorption value and calculated sorption characteristics depend on the composition of the encapsulated sorbent and adsorbate (Fig. 4). In the entire range of relative pressure the capacity of the PAN-modified sorbents for water and benzene vapors is lower than that of the initial

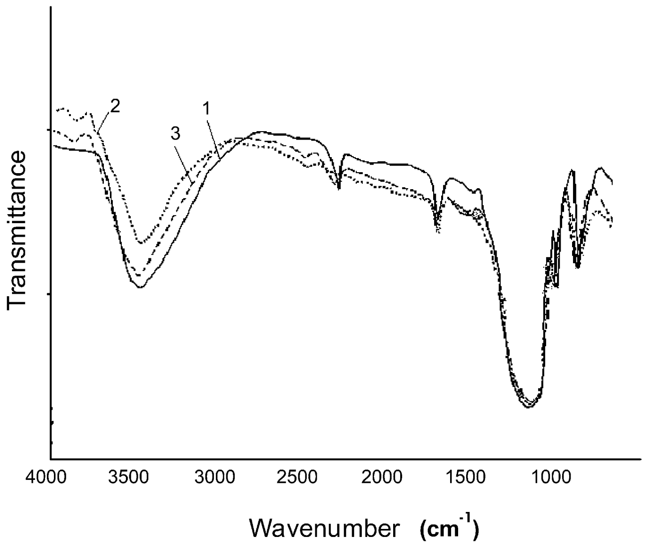

Fig. 3. FTIR spectra for (1) PAN-modified silica gel sorbent, (2) initial PMSS, and (3) PAN–PMSS (1:1) mechanical blend.

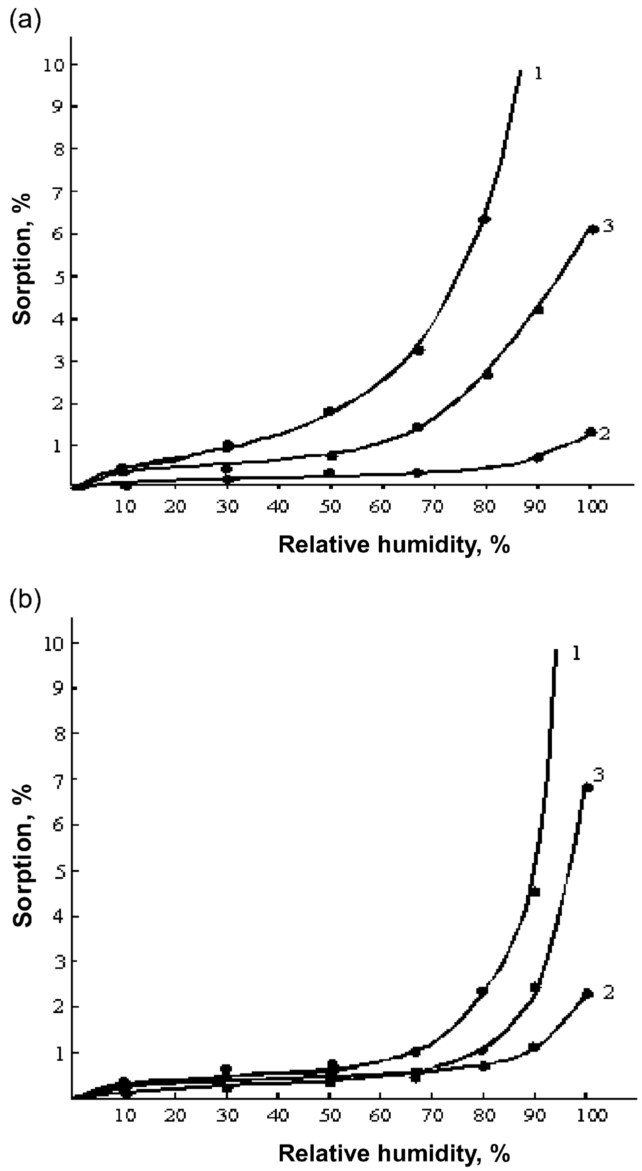

Fig. 4. Dependence of sorption (wt%) of water (a) and benzene (b) vapors by (1) PMSS, (2) PAN, (3) PAN-modified PMSS (1:1) on the relative humidity at 25 °C.

PMSS. The capacity decreases with increasing PAN modification.

4. Conclusion

The kinetic orders of reaction with regard to initiator and monomer indicate the radical nature of dominant polymerization process. XRD analysis showed that crystallinity of PAN in PAN-modified PMSS to be diminished. FTIR spectroscopy can not provide detailed information on the interaction of PAN molecules with PMSS surface, because the spectra of these compounds overlap in certain regions.

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