

Effects of Concentration and pH on the Thermosensitive Behavior of a Graft Copolymer with Polyimide Backbone and Poly(*N,N*-dimethylamino-2-ethyl methacrylate) Side Chains

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Abstract—Aqueous solutions of the graft copolymer with a polyimide backbone and poly(*N,N*-dimethylamino-2-ethyl methacrylate) side chains with a molecular mass of $M = 4.7 \times 10^5$ and a grafting density of side chains of 0.44 are investigated by light scattering and turbidimetry. Solutions are studied in a wide concentration range of 0.0008–0.0250 g/cm³ at pH values varying from 2 to 12 for each concentration. The temperature dependences of optical transmission, scattered light intensity, and hydrodynamic radii of scattering objects are obtained. It is shown that the copolymer is thermosensitive only at pH > 8.0. A decrease in acidity of the medium at a fixed concentration of the copolymer is accompanied by a decline in temperatures corresponding to the onset and end of phase separation T_1 and T_2 , leading to the narrowing of this interval. At constant pH values, temperatures T_1 and T_2 rise with solution dilution, while the phase transition interval becomes wider.

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INTRODUCTION

During the last decades, one of the actively developing directions of polymer chemistry has been related to the synthesis and investigations of branched polymer systems with well-defined structure and architecture [1–4]. Among such polymers, molecular cylindrical brushes should be emphasized, which represent graft (comblike) copolymers of regular structures and narrowly dispersed side chains over length [2, 3]. The synthesis of these copolymers offers opportunities to vary the nature and length of both backbone and side chains and the grafting density and to introduce various functional groups, making it possible to change macromolecular conformations over a wide range and, hence, to control the properties of polymer brushes and materials on their basis [2–4]. Molecular brushes are promising for practical applications in nanoengineering, for example, as containers for inorganic nanoparticles or nanofibers [5–7] as well as for preparing polymeric materials with new properties, such as supersoft elastomers [8].

Of special interest are graft copolymers with side chains that are able to respond nonlinearly to small changes in the external medium. To this end, homo- and copolymer polyelectrolytes possessing thermosensitive, photosensitive, and other practically important properties are often used as side chains [1–

4]. pH- and thermosensitive polymers belong to the so-called smart polymer systems, abruptly changing their physicochemical characteristics under external effects (variation in pressure, temperature, humidity, acidity of the medium, electric or magnetic fields, etc.).

Thermosensitive polymers were discovered in the early 1960s. They are distinguished by the presence of a lower or upper critical solution temperature. For concentrated or semidilute solutions, this phenomenon manifests itself as polymer precipitation with increasing or decreasing temperature. In strongly diluted solutions, the coil-to-globule transition upon variation in temperature is observed at the level of individual polymer chains [9]. For polymers comprising monomer units with charged groups, the temperature of phase transition is sensitive not only to concentration but also to such external stimuli as pH of the medium, ionic strength, and the presence of specific cations and anions in solution.

Thermally and pH-sensitive polymers may be used for the controlled targeted delivery of drugs, which is provided by drug release during conformational transitions and aggregation processes. Moreover, the indicated polymers may be applied as active biocompatible surfaces and for the creation of various implantable devices [10–13].

Poly(*N,N*-dimethylamino-2-ethyl methacrylate) (PDMAEM) is one of the most common and well-studied water-soluble polymers, possessing pH- and thermosensitive properties. Its tertiary amino groups may be either charged or uncharged, depending on acidity of the medium, causing pH dependences of the cloud point and low critical solution temperature (LCST). At $\text{pH} \leq 7$, amino groups are fully protonated; therefore, PDMAEM dissolves molecularly in acidic media. In alkaline media, amino groups are uncharged and the polymer exhibits thermosensitive behavior. At the same time, the cloud point and LCST of aqueous solutions of PDMAEM depend strongly on molecular mass, pH, and presence of counterions [10, 12, 14].

A convenient way to control the properties of polymeric materials is related to the synthesis of copolymers. In this case, the behavior of thermally and pH-sensitive systems containing blocks of PDMAEM or its monomer units depends on the structure and content of the comonomer. Furthermore, the characteristics under discussion are affected by the architecture of macromolecules containing PDMAEM chains as well as by the chemical nature and the mass fraction of the backbone (for graft copolymers) or the branching center (starlike polymers) [15–19].

The effect of variations in the structure of hydrophobic and hydrophilic monomer units of copolymers and in their content on the phase-separation temperature of solutions of molecular brushes was studied in [20]. The characteristics of two graft copolymers containing side chains of either a copolymer of *N,N*-dimethylamino-2-ethyl methacrylate (a thermosensitive monomer) with hydrophobic methylmethacrylate or a copolymer of hydrophilic dimethylacrylamide with hydrophobic butyl acrylate were compared. It was shown that the cloud point is lower for the molecular brushes with more hydrophobic side chains, the behavior of solutions of the polymers under investigation depending strongly on concentration. For dilute solutions, where the average distance between macromolecules is much longer than their dimensions, the heating of solution results in the collapse of macromolecules. In more concentrated solutions, where the distance between macromolecules is comparable with their sizes, supramolecular structures are formed in solution. A similar behavior was observed by K. Matyjaszewski et al. [21] for a graft copolymer with PDMAEM side chains which was obtained using poly(2-Br-isobutyroxyethyl methacrylate) as a multicenter macroinitiator. In moderately concentrated solutions (concentration $c > 5\%$), the hydrodynamic radius R_h of particles present in solution was increased with increasing temperature, which was attributed by the authors to the aggregation of macromolecules. On the contrary, in strongly diluted solutions ($0.5\% > c > 0.1\%$), R_h decreases upon heating;

this is caused by the intramolecular self-organization of macromolecules, leading to their compaction.

M. Ballauff, A.H.E. Müller, et al. [22] used the same poly(2-Br-isobutyroxyethyl methacrylate) macroinitiator to synthesize molecular brushes with PDMAEM side chains and their quaternized analog. Investigations of the behavior of the indicated graft copolymers in aqueous solutions made it possible to detect structural changes at pH from 2 to 10. At pH 7, brushes with PDMAEM side chains form wormlike rather strongly folded structures in solution. At pH 2, the macromolecules are protonated and ionized; therefore, they assume a more extended conformation, while at pH 10, they have a compact structure provided by the collapse of PDMAEM side chains.

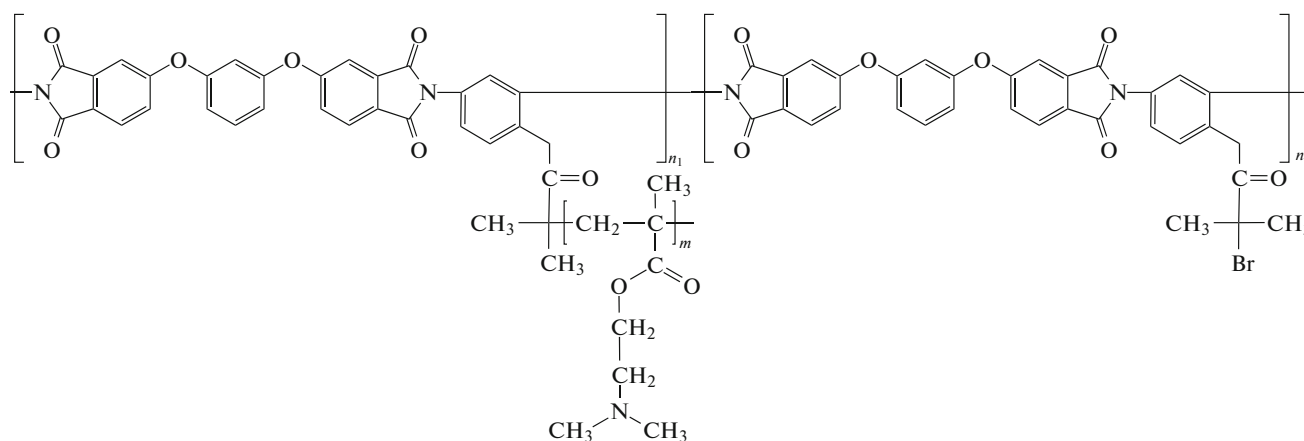
The concentrated solutions of graft copolymers containing two hydrophilic components, namely, poly(ethylene oxide) (the backbone) and PDMAEM (side chains), were studied by rheological methods [23]. It was shown that the cloud point of solutions for molecular brushes decreases with an increase in the pH of solutions and that its values are lower than those for the linear analog at the same pH values. TEM studies revealed that wormlike cylindrical structures are formed at low pH values, while the addition of NaCl salt promotes the formation of fractal structures.

Earlier, a PI-*graft*-PDMAEM graft copolymer with a polyimide backbone and PDMAEM side chains was synthesized [10]. Investigations of PI-*graft*-PDMAEM in aqueous solutions at a fixed concentration of $c = 0.015 \text{ g/cm}^3$ showed that this polymer is thermosensitive only at $\text{pH} \geq 8.9$. In alkaline media, the cloud point decreases and the phase separation interval narrows with increasing pH.

In all of the aforementioned studies, there are practically no data on the concentration dependence of solution characteristics of polymer brushes with PDMAEM side chains. As is known, the phase separation temperatures of linear thermo- and pH-sensitive polymers may change strongly upon variation in concentration, especially in the region of very dilute solutions. Therefore, the aim of the present work was to investigate the behavior of the pH- and thermosensitive PI-*graft*-PDMAEM copolymer in aqueous solutions over a wide concentration range from 0.0008 to 0.025 g/cm^3 upon variation in the pH values of medium.

EXPERIMENTAL

The synthesis of PI-*graft*-PDMAEM is described in [24]. The structural formula of its repeating units is presented below.



Note that PI-*graft*-PDMAEM macromolecules consist of two types of monomer units: units containing a grafted PDMAEM chain (the molar fraction n_1) and units of the original macroinitiator (the molar fraction n_2) which avoided the grafting reaction. The copolymer molecular mass $M = 4.7 \times 10^5$ was determined by sedimentation-diffusion analysis. A comparison of molecular masses of the copolymer and its components showed that the grafting density of side chains is rather high, $z = n_1/(n_1 + n_2) = 0.44$.

The behavior of PI-*graft*-PDMAEM in aqueous solutions was studied by static and dynamic light scattering and turbidimetry on a Photocor Complex facility (Photocor Instruments Inc., Russia) with the optical part being equipped with an ALV-SP goniometer. A Photocor-DL diode laser with a wavelength of $\lambda = 658.7$ nm served as a light source. The correlation function of scattered light intensity was processed using a Photocor-PC2 correlator with 288 channels (ZAO Anteks, Russia). The analytical procedures are described in detail in [25–27].

PI-*graft*-PDMAEM solutions in deionized water were investigated for five concentrations in the range of 0.0008–0.025 g/cm³. For each concentration, the pH was varied from 2 to 12. The acidity of the medium was changed by additions of 0.1 N HCl or 0.1 N NaOH. All solutions were filtered through Chromafil Xtra PA filters with a pore diameter of 0.45 μ m.

Experiments were carried out in the temperature range of 10–75°C. The temperature was discretely changed with the step from 0.5 to 5°C. The rate of heating was 2 K/min. The temperature was maintained with an accuracy of 0.1°C.

The measurement procedure was as follows. When the scattered light intensity I grew fast after the required temperature was reached, only dependences of I and optical transmission I^* on time t were registered. When changes in I took at most 1% of the time required for accumulation and processing of the auto-correlation function, the distribution of scattered light intensity over hydrodynamic radii R_h was also

obtained. Contributions S_i from each type of scattering particles to the total light scattering intensity were estimated from the area under the curve of intensity distribution over R_h values. The described measurements were performed at a scattering angle of 90°. Under conditions where the light scattering intensity was not varied with time, angular dependences of I , R_h , and S_i were investigated in the range of scattering angles of 40°–140°. These studies made it possible to prove the diffusion character of modes observed by dynamic light scattering and to obtain the extrapolated R_h and S_i values used for the subsequent discussion.

During experiments, intensity I changed by several orders of magnitude. In order to maintain the linearity of the device with respect to intensity, the registered light scattering was attenuated using filters (attenuation of the incident light) and diaphragms (attenuation of the scattered light), which were installed after the laser and before a photomultiplier, respectively. As a result, the measured value of I never exceeded 1.5 mHz.

It should be noted that the time needed to attain equilibrium time-invariant characteristics of solutions (light scattering intensity, optical transmission, and hydrodynamic radii of particles) was rather long, from 1500 to 15 000 s, depending on the concentration and pH of the medium. Therefore, solutions were kept for at least 1500 s at each temperature, even if the measurable characteristics were time-independent. Below, only equilibrium parameters of PI-*graft*-PDMAEM solutions will be discussed.

RESULTS AND DISCUSSION

At $\text{pH} \leq 8.0$, complete protonation of tertiary amino groups in PDMAEM side chains occurs [24], leading to the loss of polymer thermosensitivity. In the indicated pH interval, the scattered light intensity does not change with increasing temperature T for all the studied concentrations (Fig. 1a). A qualitatively similar behavior is observed for optical transmission I^* as well. This may be explained by the fact that the dimen-

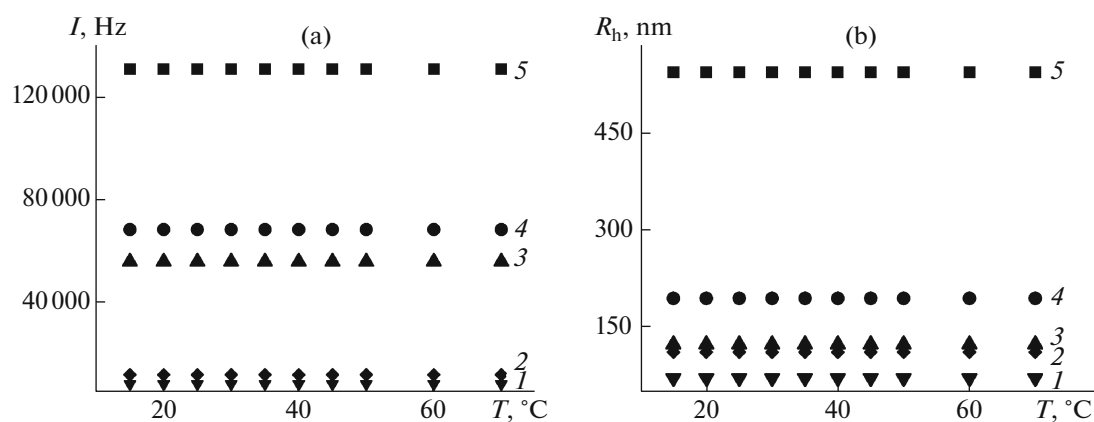


Fig. 1. Temperature dependences of (a) scattered light intensity I and (b) hydrodynamic radius R_h of PI-*graft*-PDMAEM particles present in solutions at concentrations c of (1) 0.0008, (2) 0.002, (3) 0.005, (4) 0.015, and (5) 0.025 g/cm³ and pH 7.0.

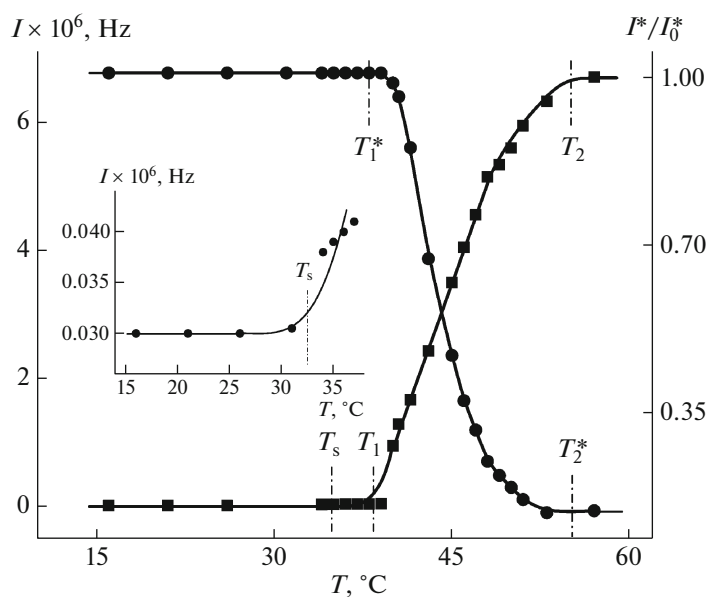


Fig. 2. Temperature dependences of scattered light intensity I and relative optical transmission I^*/I_0^* for PI-*graft*-PDMAEM solution at $c = 0.0008$ g/cm³ and pH 10.8. I_0^* is the optical transmission at room temperature. In the inset, the temperature dependence of I at $T < 38$ °C is shown. Explanations are given in the text.

sions of scattering objects remain unchanged. Under such conditions, only large particles are detected in PI-*graft*-PDMAEM aqueous solutions, with their hydrodynamic radii R_h decreasing from 540 to 70 nm upon solution dilution (Fig. 1b). Fairly large dimensions of scattering objects provide evidence for the formation of aggregates, obviously, owing to interactions between hydrophobic PI fragments of backbones of different macromolecules.

With increasing pH, the degree of protonation of amino groups of PDMAEM chains decreases, and the graft copolymer acquires thermosensitivity at pH > 8.

This conclusion follows from analysis of the temperature dependences of characteristics of PI-*graft*-PDMAEM solutions presented in Figs. 2–4 (lines describing dependences in Figs. 2–6 are drawn “by eye”).

In an alkaline medium, the dependences of scattered light intensity I and I^* on T may be tentatively divided into four regions (Fig. 2). In the first region, at low temperatures, the considered characteristics do not change. Two modes, that is, two kinds of particles, were detected in solution by dynamic light scattering. Their hydrodynamic radii R_f (the fast mode) and R_s

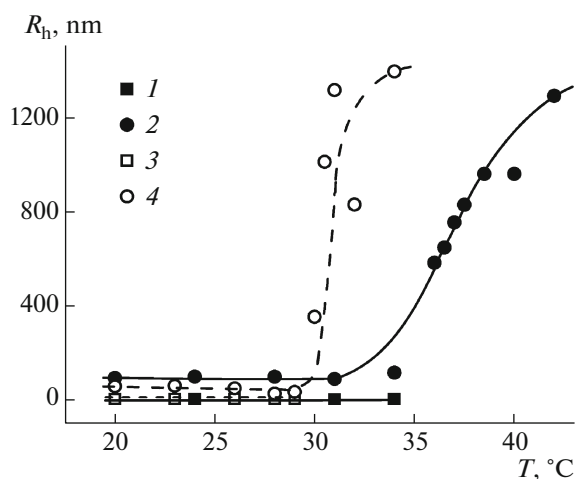


Fig. 3. Temperature dependences of the hydrodynamic radius of (1, 3) fast R_f and (2, 4) slow R_s modes for PI-*graft*-PDMAEM solutions at (1, 2) $c = 0.002 \text{ g/cm}^3$ and pH 12.3 and (3, 4) $c = 0.025 \text{ g/cm}^3$ and pH 12.5.

(the slow mode) differ by several times (Fig. 3). The value R_f remains virtually constant upon variation in the copolymer concentration and pH of the medium, its mean value at different concentrations and pH being 8 nm. As was shown in [24], particles responsible for the fast mode are isolated PI-*graft*-PDMAEM macromolecules, with their small sizes being due to the collapse of backbone PI chains that are insoluble in water.

The slow mode reflects the presence of aggregates in solutions which are similar to those formed in the solutions of PI-*graft*-PDMAEM at pH < 8. At room temperature, R_s shows no systematic changes upon variation in acidity of the medium at all concentrations. At a fixed pH, a nonmonotonic change in the size of aggregates is observed: as concentration c is decreased from 0.025 to 0.015 g/cm^3 , radius R_s declines on average by a factor of 1.5, while upon a further dilution it increases by a factor of 2–4 at various pH values. There may be several reasons for this nonmonotonic change in the hydrodynamic sizes of aggregates, or rather their diffusion coefficient D_s , with concentration. In particular, it may be assumed that the concentrations $c > 0.015 \text{ g/cm}^3$ are in the region of semidilute solutions. It is worth noting that, in an organic solvent (chloroform), the intrinsic viscosity $[\eta] = 59 \text{ g}^{-1} \text{ cm}^3$ [24]; that is, the value $c = 0.015 \text{ g/cm}^3$ is close to the overlap concentration of molecular coils, at which the character of the concentration dependence of the diffusion coefficient changes sharply. At the same time, it should be recalled that the thermodynamic qualities of water and chloroform for PI-*graft*-PDMAEM are substantially different. Moreover, upon a decrease in concentra-

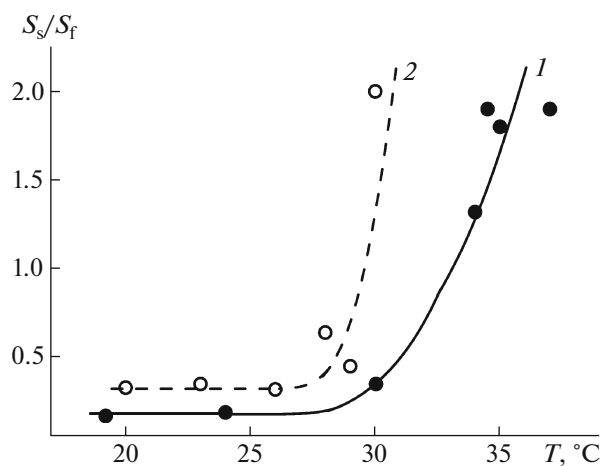


Fig. 4. Temperature dependence of the ratio S_s/S_f for PI-*graft*-PDMAEM solutions at (1) $c = 0.002 \text{ g/cm}^3$ and pH 9.5 and (2) $c = 0.025 \text{ g/cm}^3$ and pH 12.5.

tion, disaggregation processes are possible and lead to changes in the dependence of D_s on c .

Within the considered temperature range, the contributions of different types of particles to the total light scattering do not change, and this finding reflects the constancy of the ensemble of scattering objects. Note that, at all pH values and copolymer concentrations, the contribution of the fast mode S_f exceeds noticeably that of the slow mode S_s ; at room temperature, S_s/S_f is always < 0.5 (Fig. 4). This circumstance reflects the fact that the collapsed polymer macromolecules prevail in the investigated solutions. Indeed, for particles of any shape, the intensity of light scattering strongly depends on their sizes R_i and increases quickly with the growth of R_i .

At temperature T_s , intensity I starts ascending slowly, while the optical transmission I^* remains constant (Fig. 2). The hydrodynamic dimensions of scattering objects do not change either (Fig. 3), and the increase in I is due to change in the ratio S_s/S_f , which rises with temperature (Fig. 4); that is, the fraction of aggregates in solution increases. This behavior is observed up to temperature T_1 .

Within the next temperature range (from T_1 to T_2), the heating of the solution is accompanied by the fast growth of I . At temperature T_1^* , I^* starts decreasing. For all the investigated solutions, temperatures T_1 and T_1^* coincide within 0.5°C (Fig. 2).

Changes in light scattering intensity and optical transmission at $T > T_1$ (or T_1^*) are related to worsening of thermodynamic quality of the solvent owing to deprotonation of the amino groups of side chains. In this range, the growth of the hydrodynamic radius of

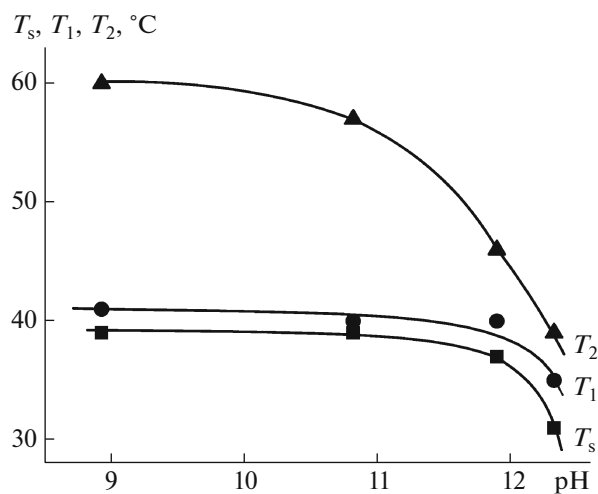


Fig. 5. Dependences of temperatures T_s , T_1 , and T_2 on the pH of medium for PI-*graft*-PDMAEM solutions at $c = 0.0008 \text{ g/cm}^3$.

aggregates R_s is observed (Fig. 3) together with the redistribution of the number of scattering objects, namely, an increase in the fraction of supramolecular structures at the cost of a decrease in the fraction of macromolecules. Therefore, it may be assumed that the growth of the sizes of aggregates is related to both their merging and the addition of single macromolecules. At temperature T_2 , the fast mode (isolated macromolecules) is not observed, while the intensity of light scattering reaches its highest value. At temperature T_2^* , the optical transmission drops to almost zero even in the most diluted solutions. Within the entire ranges of copolymer concentrations and pH values, relation $T_2 \geq T_2^*$ is observed with the difference between the temperatures under consideration being at most 2°C . The temperature range from T_1 to T_2 (or from T_1^* to T_2^*) should be considered as the phase-separation range.

Within the fourth temperature interval, above T_2 , light scattering is not classic, because the dimensions of scattering objects are comparable to the incident light wavelength and the quantitative analysis of experimental dependences is impossible. It should only be noted that, at $T > T_2$, the intensity of light scattering and the hydrodynamic radii of aggregates R_s decline for the majority of the studied solutions probably owing to compaction of aggregates upon worsening of the thermodynamic quality of the solvent with temperature.

As was mentioned above, the degree of protonation of amino groups depends on the acidity of the medium. Consequently, it may be expected that the phase-separation temperature and the width of this interval also change with variation in pH. In Fig. 5, the

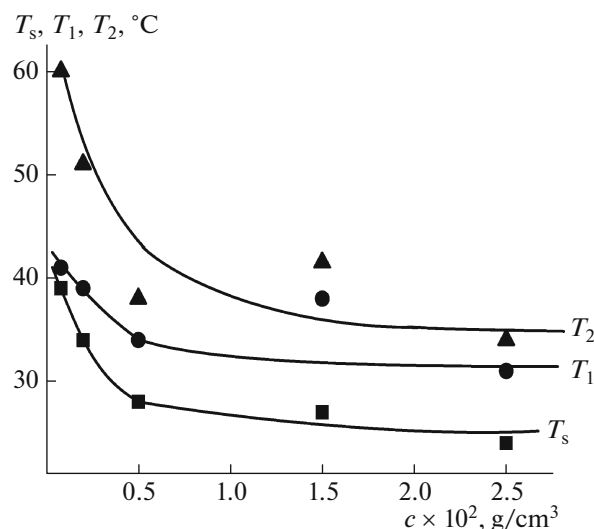


Fig. 6. Concentration dependences of temperatures T_s , T_1 , and T_2 for PI-*graft*-PDMAEM solutions at pH 9.

dependence of temperatures T_s , T_1 , and T_2 on the pH of the medium at a concentration of 0.0008 g/cm^3 is presented as an example. It is clearly seen that the named temperatures decrease with the basicity of the medium, while the difference $T_1 - T_s$ is virtually constant throughout the studied pH range. Temperature T_2 decreases with increasing pH much faster than T_1 ; that is, the phase separation interval narrows sharply with a decrease in acidity, for example, at $c = 0.0008 \text{ g/cm}^3$ from 20 to 4°C .

Similar features were also observed for other investigated concentrations. Furthermore, as expected, a fairly strong concentration dependence of characteristic temperatures of PI-*graft*-PDMAEM solutions is observed. Figure 6 shows changes in temperatures T_s , T_1 , and T_2 upon variations in c at pH 9. At all the remaining pH values, qualitatively similar dependences are obtained. The scatter of experimental points on these dependences is rather high (the accuracy of determination of T_s , T_1 , and T_2 does not exceed 2°C). However, as is seen at all pH values, dilution is accompanied by both an increase in the considered temperatures and widening of the phase-separation interval. A similar dependence is characteristic of thermosensitive polymers in the range of low concentrations [26, 28–30].

CONCLUSIONS

Using the method of dynamic light scattering, it is shown that the graft copolymer PI-*graft*-PDMAEM is pH- and thermosensitive in aqueous solutions only above a certain pH value. At $\text{pH} \leq 8.0$, PI-*graft*-PDMAEM is not thermosensitive. In neutral and acidic media, large aggregates are observed in solu-

tions throughout the investigated ranges of temperatures and concentrations. The indicated supramolecular structures are formed owing to interactions between hydrophobic PI fragments of backbones of different macromolecules.

PI-*graft*-PDMAEM becomes thermosensitive at $\text{pH} > 8.0$. This fact is obviously due to a decrease in the degree of protonation of amino groups of PDMAEM side chains and, hence, worsening of solubility of the graft copolymer. An increase in pH at a fixed concentration leads to a decrease in the temperatures corresponding to the onset and end of phase separation T_1 and T_2 and to the narrowing of this interval. At a constant $\text{pH} > 8.0$ within the investigated concentration range, the dilution of solutions is accompanied by an increase in temperatures T_1 and T_2 and widening of the phase-transition interval.

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