ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

4 (64)

ОКТЯБРЬ – ДЕКАБРЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDK 541.64: 539.2

A. A. TALTENOV, G. K. SHAMBILOVA

Dosmukhamedov Atyrau State University, Atyrau, Republic of Kazakhstan
E-mail: shambilova_gulba@mail.ru

PHASE STATE AND RHEOLOGICAL PROPERTIES OF SOLUTIONS OF POLYAMIDE BENZIMIDAZOLE IN DIMETHYLACETAMIDE

Abstract. The article explores solutions poliamidbenzimidazole used to obtain high-strength heat-resistant fibers and reinforced plastics produced by using precipitants. Investigated rheological properties 5% of the reaction mixtures and solutions poliamidbenzimidazole with polysulfone in DMAA with addition of 3% LiCl, to improve solubility of the polymer. Is constructed part of the phase diagram corresponding to the investigated area of concentration. Shown that viscosimetric and optical methods clearly indicate the existence of a thermodynamic transition in the system poliamidbenzimidazole-DMAA. Also were investigated viscosity properties of mixtures of the solutions poliamidbenzimidazole with PSF in DMAA at different temperatures.

Keywords: poliamidbenzimidazole, a rigid chain polymer, the liquid crystal phase, dimethylacetamide, phase diagrams, rheological properties, solutions of polymer, viscosity.

Introduction. Polyamidobenzimidazole (PABI) is a typical representative of rigid-chain polymers. It is used to produce heat-resistant high-strength fibers and reinforced plastics, including in a mixture with conventional thermoplastics [1]. Sulfuric acid solutions of PABI can form a liquid-crystalline (LC) phase, the nematic order is retained in the PABI after the polymer is separated from the solution by the action of precipitators. At the same time, in the solutions in dimethylacetamide (DMAA) containing up to 20% of the polymer, the formation of the LC phase was not observed due to the fact that the rigidity of the polymer chain in this solvent decreases [2]. However, this does not exclude the appearance of an LC state at higher concentrations of PABI.

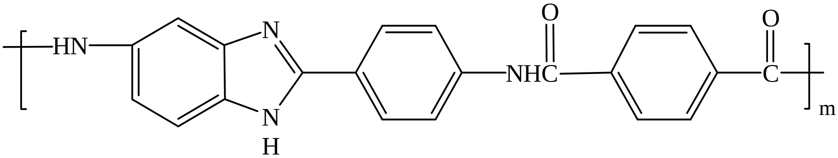
Fibers based on PABI are obtained by spinning from reaction solutions (polycondensation syrups) directly formed during its synthesis, in particular in DMAA medium, by a "wet method", i.e. using precipitators at room temperature. In this case, the conditions for spinning fibers from solutions are determined by the evolution of the phase states of solutions through the stages of the process (precipitation, gel fiber extraction, drying, heat treatment, etc.). Hence the problem arises of estimating the rheological properties of PABI solutions in connection with its phase state. The main role in this is played by the temperature factor, since the concentration of PABI solutions can vary only within very narrow limits.

As already mentioned above, the viscosity properties of solutions of rigid-chain polymers are very sensitive to phase transitions. This is particularly pronounced in the formation of the LC phase [3] or in the amorphous separation of solutions or mixtures of polymers. Not being a thermodynamic parameter, the viscosity, however, turns out to be a sensitive indicator of phase transformations in solutions.

EXPERIMENT

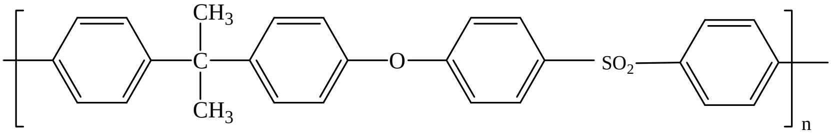
Proceeding from the above, the following problems were solved in the article. First, the study of the rheological properties of 5% reaction solutions of PABI and its mixtures with polysulfone (PSU) in DMAA supplemented with 3% LiCl, improving the solubility of the polymer [4], and, secondly, the detection and description of temperature transitions in these systems that are associated with the phase changes occurring in the system when it is heated.

Characteristics of objects. The PABI sample of the following chemical structure was used:



Its molecular weight was determined from the intrinsic viscosity [η] measured at 20°C. in DMAA supplemented with 3% LiCl. It is [η] = 7.2 dl/g. When calculating using the data of [4], this value of the intrinsic viscosity corresponds to a average viscosity molecular weight of $7.1 \cdot 10^4$.

As a second component of the mixture PSU obtained on the basis of diphenylolpropane and 4-dichlorodiphenylsulfone, was used. The structural formula of this polysulfone is:



Estimates of the molecular weight of the sample used, based on its intrinsic viscosity, gave a value of $4 \cdot 10^4$, i.e. the value is close to the molecular mass of the PABI sample.

Solutions containing 5% PABI were obtained directly during polymer synthesis in DMAA + 3% LiCl. From this, solutions of lower concentration were prepared by dilution. Solutions of PABI-PSU mixtures containing a total of 5% of these polymers, but with a different ratio of components, were obtained by adding to the initial 5% PABI solution the necessary amounts of an equiconcentrated PSU solution.

All PABI solutions remained clear and stable at room temperature for at least 6-8 months under conditions of their protection against air moisture. According to the measurement of their turbidity spectra [5, 6], these solutions are practically homogeneous systems. Estimates of the size of heteroformations showed that their effective diameter does not exceed 0.02 microns, which corresponds to the lower limit of the sensitivity of the method.

The PABI-PSF systems in DMAA with the addition of 3% LiCl remained visually transparent for several tens of hours (depending on the ratio of the polymers). However, later they became turbid. This indicates that these systems can be considered only as kinetically compatible, but from the thermodynamic point of view the components in these systems are incompatible.

RESULTS AND DISCUSSION

Rheological properties and phase state of PABI solutions. In figure 1 presents experimental data on the dependence of the effective viscosity of η 5% PABI solutions on the shear rate ў at various temperatures.

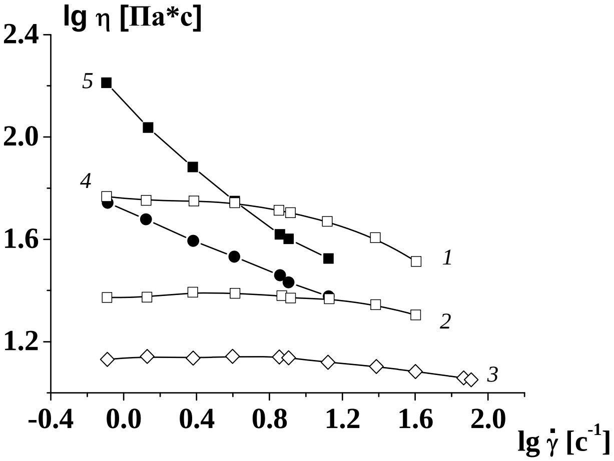


Figure 1 – Curves of the flow of 5% PABI solutions in DMAA at different temperatures: 20 (1), 60 (2), 108 (3), 116 (4), 121 ° C (5)

In all cases, a non-Newtonian flow characteristic of polymer solutions is observed with a drop in the effective viscosity with increasing shear rate. However, experimental data also demonstrate another significant difference in the behavior of solutions at low temperatures (curves *1*-*3*) and at elevated temperatures (curves *4* and *5*) with a change in the character of the rheological properties between 108 and 1160C. In the low-temperature region, a region of Newtonian flow is reached in a rather wide range of shear rates, which indicates that the structure of the solution remains unchanged. An increase in temperature in this range leads, as usual, to a decrease in viscosity. Qualitatively, in a similar way, the change in η with the shear rate and temperature also occurs in the case of solutions with a lower PABI content.

Of particular interest is the high-temperature region. As can be seen, in this case the tendency to reach a region of constant (the highest Newtonian) viscosity vanishes when the shear rate decreases in the region of low velocities, as is observed at lower temperatures. Similar behavior is observed at other concentrations of PABI.

It was found that the relationship between the speed and the shear stress of the system in this case (i.e., in the high-temperature region) is well described by the well-known Casson equation [4]:

$$\tau^{0.5} = \tau_Y^{0.5} + \alpha\dot{\gamma}^{0.5} \qquad (2.8)$$

where τ – is the shear stress; τ_Y – is the fluidity limit; α – is a parameter that depends on the composition of the system.

The applicability of this equation to the systems studied is illustrated in figure 2. As you can see, the experimental points really lie on the straight lines constructed in the coordinates of the Kasson equation. The Kasson equation is widely used to represent the rheological properties of many heterophase low- and high-molecular systems, such as paints containing a pigment, greases, polymers filled with active fillers. A characteristic feature of all these systems is the presence of a structural framework in them, subject to failure at shear stresses exceeding the fluidity limit, which is thus a measure of the strength of the solid structure of the substance. For a 5% solution of PABI, the value of τ_Y at 118°C turned out to be 78.0 Pa.

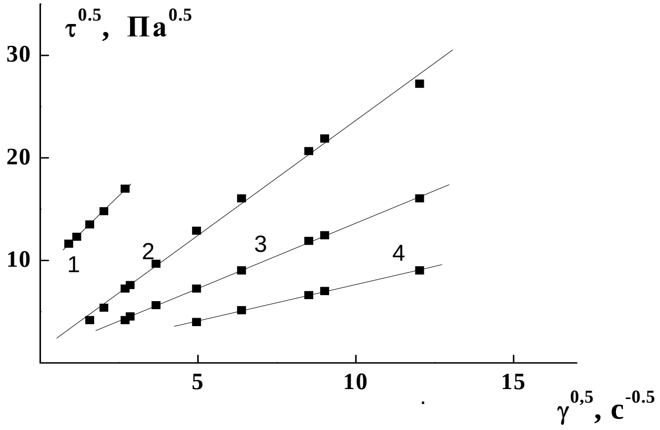


Figure 2 – Experimental data of a mixed 5% solution of PABI and PSU in DMAA of the dependence of shear stress on velocity in the coordinates of the Casson equation. The ratio of PABI: PSU = 100: 0 (1), 90:10 (2), 70:30 (3), 50:50 (4). The temperature is 118°C

Thus, if in the low-temperature region the systems studied were solutions, then upon transition to the high-temperature region they undergo an obvious transition with formation of a structure and transformation into visco-plastic bodies possessing a definite and quite noticeable strength of structure. At the same time, it should be noted that the partial replacement of the PABI on the PSU (sequential transition from graph *1* to graphs *2*, *3* and *4*) leads to a decrease in the yield strength, i.e. structures formed with the participation of PSU , have less strength than PABI.

For completeness of the viscous properties of PABI solutions, the obtained data on the concentration dependence of viscosity are also given. This is done in figure 3, where the concentration dependence of the activation energy of viscous flow is also shown. The data presented here relate to the Newtonian flow region, i.e. to systems in an equilibrium state.

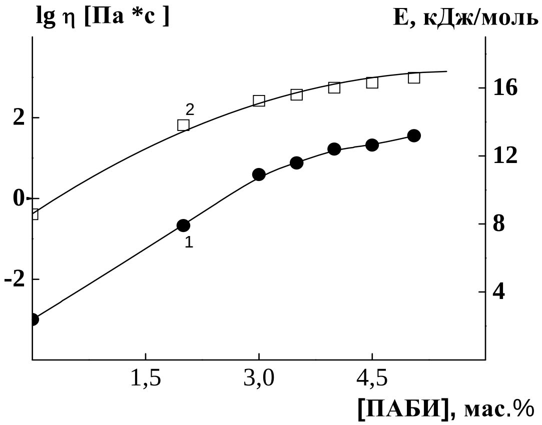


Figure 3 – Dependence of the viscosity and activation energy of the viscous flow of PABI solutions in DMAA in the region of existence of homogeneous systems

As can be seen, when passing from a pure solvent to a 5% solution, the viscosity significantly increases – by more than four decimal orders, which is typical for solutions of rigid-chain polymers. Comparison of the viscous properties of 5% solutions of PABI and flexible non-polar polyisobutylene in isooctane [7, 8] shows that for an equal degree of polymerization of both polymers, the viscosity of the 5% PABI solution is ~$3 \cdot 10^4$ times higher than the solution of polyisobutylene. This is characteristic of rigid-chain polymers and indicates a relatively high degree of structuring of PABI solutions with the formation of apparently quite stable associates. Nevertheless, judging by the stability of the rheological properties, it can be said that the PABI-DMAA system in this composition region forms an equilibrium solution.

In accordance with the high rigidity of the PABI macromolecules, and the activation energy of the flow of the 5% PABI solution (figure 1), calculated from the data of Fig. 3 in the region ~ 20-100°C using the usual exponential equation of the Arrhenius equation type, it turns out to be ~2 times more than in the case of a flexible-chain polymer solution. These rheological data confirm the initial idea that PABI is a rigid-chain polymer.

For the purposes of this study, in which the evolution of rheological properties is closely related to the phase state of the system, the analysis of the temperature dependence of viscosity is of fundamental importance. From Fig. 1 that there are certain anomalies here, since, when passing through a critical temperature region, the viscosity can decrease. This question was considered in detail in [9, 10].

The main experimental result related to this field of research is the observed effect of an extreme change in the viscosity of the PABI-DMAA system with a clearly pronounced minimum observed in the same temperature range as in Fig. 1 there is a change in the character of the rheological behavior of the system with the transition from the state of a viscous liquid to a viscoplastic medium. This effect is shown in figure 4.

It should be noted that this graph shows the values of the effective viscosity at a sufficiently high shear rate when it comes to a structure partially destroyed by deformation. Naturally, such a dependence can not be constructed for the low-stress region, since there is no flow of the systems under consideration in the high-temperature region.

The lower point of the "fracture" -the transition from the falling branch of the temperature dependence of the viscosity to the increasing branch of this dependence will be denoted as T_{min}. The physical meaning of the existence of the point T_{min} is quite obvious: this is a transition between two different states of the system, which leads to a change in its structure and corresponding changes in the rheological properties.

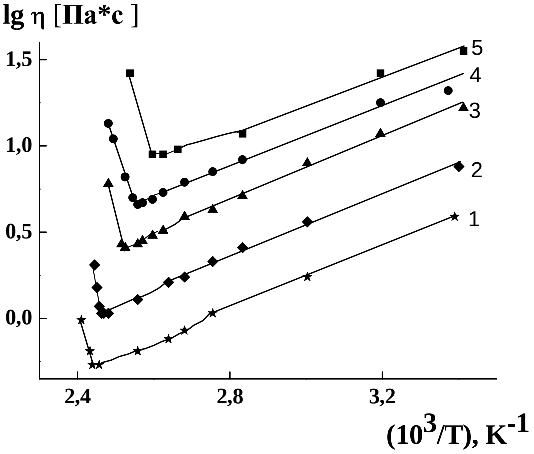


Figure 4 – Temperature dependences of the viscosity of the PABI-DMAA system at a polymer concentration of 3.0 (1), 3.5 (2), 4.0 (3), 4.5 (4) and 5.0 wt. %. Shear rate = 13.5 s^{-1}

Changes in rheological properties are as follows: a viscous liquid is transformed into a viscous plastic medium, which at the same time begins to show elasticity. The latter is expressed by the fact that, at elevated temperatures, the Weissenberg effect is clearly pronounced [3, 4]: the sample under study begins to "crawl" out of the working gap between the stationary and rotating surfaces in a rotational instrument.

The drop in viscosity with increasing temperature in the low-temperature region seems quite trivial, but its growth after passing through the point T_{min} is a specific feature of solutions of rigid-chain polymers. Previously, a similar effect was described for some other solutions of rigid-chain polymers - aqueous solutions of methylcellulose and polymethacrylic acid [11] and was associated with gelation of solutions – the formation of a non-flowing gel.

The data in figure 4 allow us to construct a section of the phase diagram corresponding to the investigated concentration region. It is shown in figure 5.

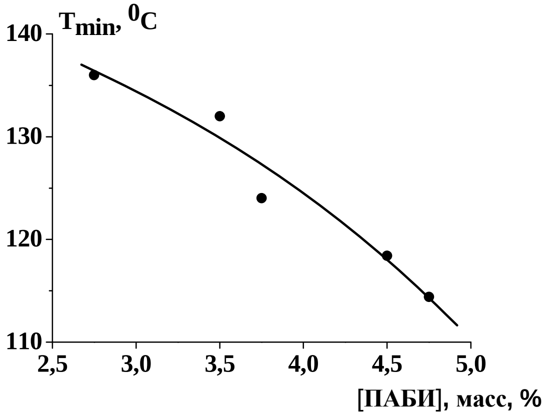


Figure 5 – Section of the phase diagram showing the concentration dependence of the transition temperature from a viscous liquid to a viscoplastic medium for the PABI-DMAA system

Studies have shown that an increase in viscosity with increasing temperature after passing through a minimum is reversible, and when cooled, the viscosity reaches its initial value. This means that the transition shown in figure 5, is reversible and can be regarded as a true thermodynamic transition.

An additional independent evidence of the existence of a transition at T_{min} is the results of measurements of the temperature dependence of turbidity θ. The corresponding experimental data are shown in figure 6.

These data clearly show the existence of a transition at a temperature T_{tr}, detected by increasing the turbidity of the system, which indicates the appearance of heterogeneity of the system due to the formation of a new phase.

Some discrepancies in the values of the transition temperature, found when comparing figures 4 and 6 are explained by the features of the applied techniques and, in particular, by the kinetic nature of the transition inherent in polymer systems.

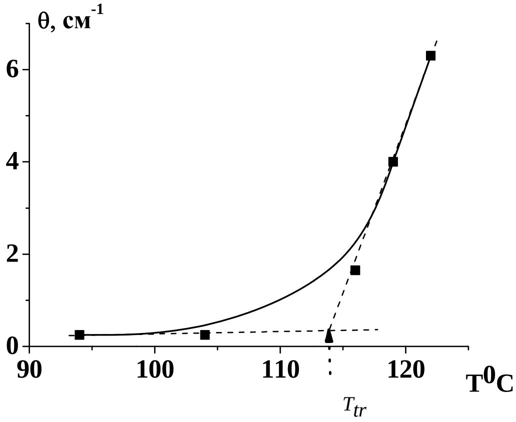


Figure 6 – Dependence of turbidity of 5% PABI-DMAA systems on temperature

A direct proof of the heterogeneity of the structure in the PABI-DMAA system formed in the high-temperature region is the microphotography of the systems (figure 7).

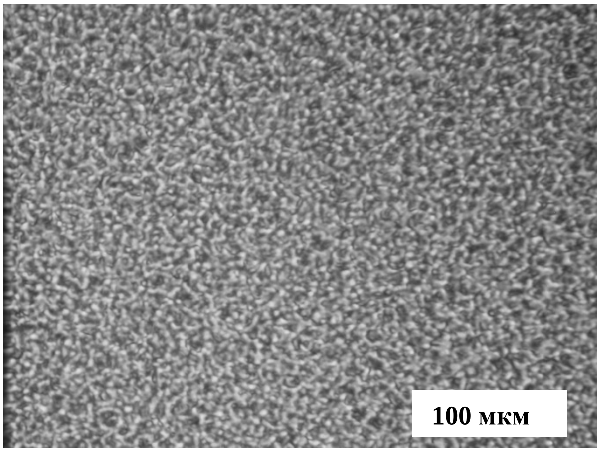


Figure 7 – Microphotography of the 5% PABI-DMAA system at 128^{0}C

The particles visible on this photomicrograph with average diameters and lengths of the order of 5 and 25 μm, respectively, are already secondary formations formed as a result of agglomeration of the polymer phase during the syneresis of the solvent. Their size, in principle, should depend on the heating mode. As for the manifestation of birefringence by these particles, this can be caused either by the mesophase nature of the highly concentrated system or by the photoelastic effect known for the polymer jelly effects due to shrinkage phenomena in the process of syneresis.

Thus, both viscometric and optical methods clearly indicate the existence of a thermodynamic transition in the PABI-DMAA system.

If we follow the Papkov classification [11], then the detected transition should be treated as a liquid-gel transition. At the same time, the mechanism of decay of the systems under study when heated into separate phases requires special discussion. Such a discussion is connected with some general considerations based on the known for many systems polymer-solvent and polymer-polymer phase decay by the spinodal mechanism [11]. In this case, as the binodal is approached, an anomalous increase in the viscosity and activation energy of the flow is observed, which is believed to be due to the formation of associates of macromolecules [12]. The transition to the metastable region between the binodal and the spinodal can be accompanied by a strong decrease in viscosity. After passage of the spinodal and completion of the decomposition of the system into separate phases, the viscosity is determined by the morphology of the mixture, and the viscosity of its components and, as a rule, increases due to gelling.

As for the PABI-DMAA system under investigation, it was established in [13, 14] that the initial solutions of PABI containing up to 20% of the polymer, as well as the fibers obtained from them, are in the amorphous state before the heat treatment stage. This suggests that the decay of PABI solutions upon heating should also take place in a liquid-liquid manner, i.e. by the mechanism of amorphous nucleation. It should also be added that the character of the section of the phase diagram shown in figure 5, can be considered as an additional argument in favor of the amorphous separation of the system. These experimental results suggest that the PABI-DMAA system has a lower critical mixing temperature.

It should be taken into account that PABI, being a rigid-chain polymer, tends to form an LC phase in a number of solvents. Therefore, it can be assumed that on the threshold of amorphous delamination, when the DMMA content decreases, precipitation forms mesophase meshes of anisodiametric form.

The loss of the solubility of PABI in DMAA at elevated temperatures appears to be due to the breakdown of the hydrogen bonds between the amide groups of the polymer and the solvent, especially when the temperature rises above 80°C. As is known [15], there is also a significant drop in the intrinsic viscosity of PABI solutions in DMAA. LiCl, capable of strong interaction with both components of the solution, should lead to the formation of complexes, whose strength decreases with increasing temperature, and at certain temperatures they decay. Both effects: the destruction of the network of H-bonds and the decomposition of complexes lead to loss of solubility of PABI in a complex solvent and, as a consequence, to phase disintegration of solutions.

Solutions of mixtures of polyamidobenzimidazole with polysulfone. Along with PABI solutions, the viscosity properties of solutions of PABI mixtures with PSU in DMAA at different temperatures were studied. In the mixtures studied, the total concentration of polymers in the system was 5%, and the ratio of polymer components varied widely.

As an example, figure 8 shows the viscosity versus shear rate at different temperatures for solutions with a ratio of PABI to PSU equal to 1: 1.

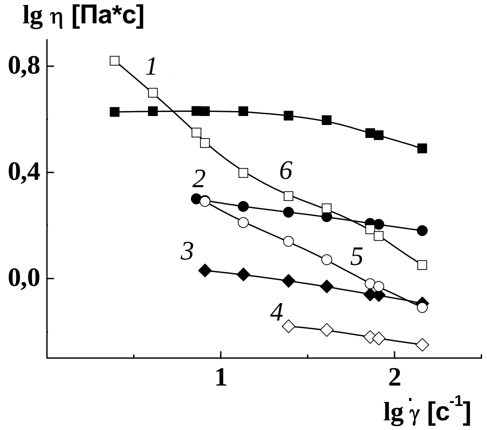


Figure 8 – Dependence of viscosity on the shear rate of PABI mixtures: PSU = 1: 1 in DMAA at temperatures of 20 (1), 60 (2), 95 (3), 121 (4), 124 (5), 134°C (6)

As can be seen, the nature and position of the curves in figure 8 are completely similar to that which was obtained for solutions of pure PABI and is shown in Fig. 1. It is obvious that at temperatures up to about 100°C the systems under consideration behave as non-Newtonian fluids whose viscosity decreases with increasing shear rate. However, this effect is generally small. In addition, the viscosity of the solutions decreases with increasing temperature. Just as in the case of solutions of pure PABI, when a certain temperature threshold is exceeded, the behavior of the solutions changes and the transition from a viscous liquid to a viscoplastic body with an explicit yield strength. The nature of the change in the yield stress as a function of the relative content of PABI and PSF in the mixture was shown in figure 2.

Practical and theoretical interest is the change in the viscosity of solutions of mixtures as a function of the ratio of PABI:PSF in the low-temperature (homogeneous) region. The corresponding experimental data are shown in figure 9.

It is important to compare the viscometric data with the results of measurements of the dependence of the activation energy of viscous flow in the single-phase region of solution states on the content of polymer components. This dependence is shown in figure 10.

The obtained dependence of the activation energy of the viscous flow on the composition of the mixture clearly demonstrates that three regions can be distinguished on it. If we assume that the values of the activation energy reflect the flow mechanism, then it can be assumed that in the concentration range of ~0-30% of the PSU, the continuous phase is a solution of PABI in DMF, and in the concentration range of ~70-100%, the PSU is a PSU solution. In the inter-

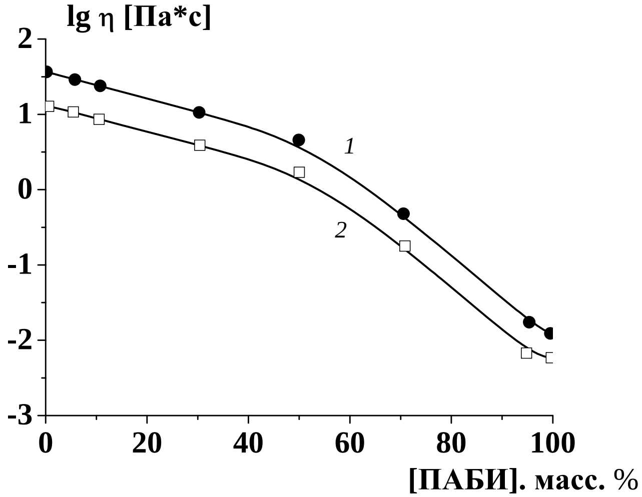


Figure 9 – Dependence of viscosity at 20°C (1) and 80°C (2) on the concentration of PSA in mixture with PABI. The shear rate is $\dot{\gamma}$ =13.5 s^{-1}

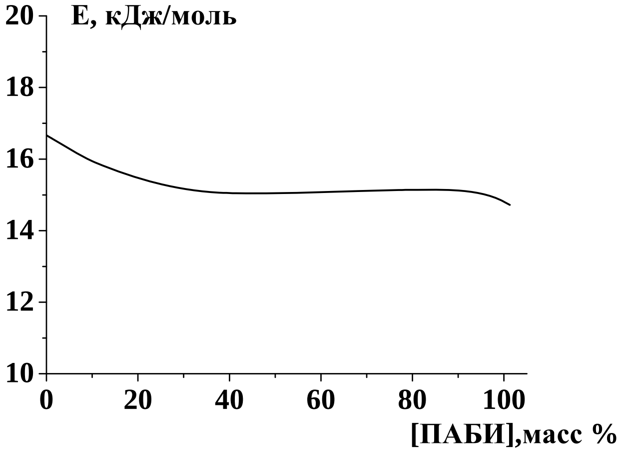


Figure 10 – Dependence of the activation energy of viscous flow on the concentration of PSU in a mixture with PABI. The shear rate is $\dot{\gamma}$ =13.5 s^{-1}

mediate region of the compositions (in which the activation energy remains practically constant), the solutions of both polymers probably form a system of coexisting phases.

Similarly, like the solutions of pure PABI, the temperature dependences of the viscosity of solutions of mixtures with a different ratio of components behave (figure 11).

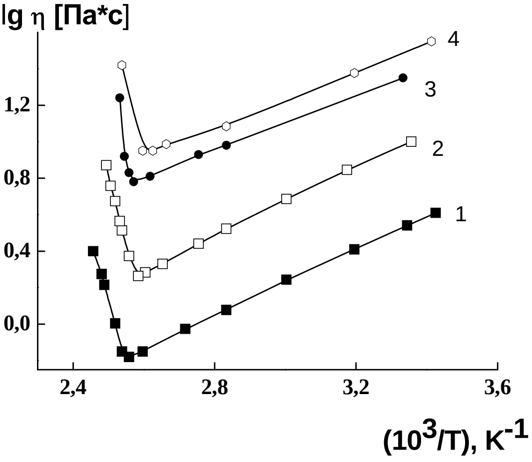


Figure 11 – Temperature dependences of the viscosity of solutions of PABI-PSU mixtures in DMAA. The content of PSU in the mixture: 50 (1), 30 (2), 10 (3), 0% (4). Shear rate $\dot{\gamma}$ = 13.5 s^{-1}

Here, also, the temperature dependence of the viscosity is anomalous with the existence of two regions: a low-temperature one, in which the standard (Arrhenius) temperature dependence of viscosity and the high-temperature dependence with an anomalous temperature dependence of viscosity take place. The minimum points are the phase transition region. The transition temperature T_{min} remains practically the same for systems with different component ratios. This experimental fact, as well as the monotonous decrease in the yield stress τ_Y with the addition of PSU to PABI, should apparently be considered as evidence that PSF does not participate in a specific interaction with the components of the solution and should be considered only as a modifying "rheological additive" which reduces the viscosity of the system as a whole.

Thus, from the experimental data obtained, it follows that the phase diagrams of PABI solutions in DMAA in the studied range of compositions (up to 5% polymer concentration) are characterized by the presence of a lower critical mixing temperature. Addition of up to 50% by weight of the polymer to the polymer. PSU does not affect this transition temperature, but leads to a significant decrease in the viscosity of the system, playing the role of a "modifier" of the viscous properties of the system.

REFERENCES

[1] Kotomin S.V., Molecular composites and blends polyamidbenzimidazol-polyarilensulfon // VysokomolekulyarnyeComm. Ser. A, 2003, 45, 3, 460-467 (in Rus.).

[2] Iovleva M.M., Banduryan S.I. Some ways to achieve a liquid crystal structure in the systems spinning polymer-solvent // Chem. Fiber. 1995, 2, 9-12 (in Rus.)

[3] Papkov S.P. Rheological properties of abisoptropic poly-(para-benzamide) solutions // J. Polymer Sci.: Polymer Phys Ed. 1973, 12, 9, 1753-1770.

[4] Iovleva M.M. Phasediagramsoffiber-formingpolymers // Chem. Fiber, 2000, 4, 20-25 (in Rus.).

[5] KleninV.I. Thermodynamics of systems with flexible chain polymers / Ed. Saratov State University, 1995 (in Rus.)

[6] Smirnova V.M., Iovleva M.M., Methods range turbidity and research solutions of fiber-forming polymers. M.: NIITEKHIM, 1980. 40 p. (in Rus.).

[7] Dreval' V.E., Malkin A.Ya., Vinogradov G.V., Tager A.A., Effect of the solvent nature on the rheological properties of concentrated solutions of different polymers // Europ. Polymer J. 1973, 9, 1, 85-99.

[8] Dreval' V.E., Malkin A.Ya., Botvinnik G.O., Approach to genralization of concnetration dependencies of zro-shear viscosities in polymer solutions // J. Polymer Sci.: Polymer Phys Ed. 1973, 11, 6, 1055-1076.

[9] Shambilova G.K. Anomalous temperature dependence of the viscosity of solutions of rigid polymers as a result of the phase transition // Vestnik KazNTU. 2009. 6(76). 182-184 (in Rus.).

[10] Shambilova G.K., Dreval' V.E., Kotomin S.V., Kulichikhin V.G. The viscosity and thermal transitions in solutions polyamidbenzimidazole and mixtures there of with polysulfone in dimethylacetamide // Vysokomolekulyarnye Comm. Ser. A, 2010, 52, 1, 3-10 (in Rus.)

[11] Papkov S.P. The gelatinous state of polymers. M.: Chemistry, 1974. 450 p. (in Rus.).

[12] Kuleznev V.N. Association of macromolecules and its effect on the mutual solubility of polymers // Vysokomolekulyarnye. Comm. Ser. B, 1993, 35, 8, 1391-1402 (in Rus.).

[13] Iovleva M.M., Konovalova L.Ya., Negodyaeva G.S., Sokira A.N., Avrorova L.V., Volokhina A.V., Papkov S.P. Structural features of polymers detected by the method of water vapor sorption // Vysokomolekulyarnye. Comm. Ser. B, 1983, 25, 10, 776-778 (in Rus.).

[14] Smirnova V.N., Prozorova G.E., Iovleva M.M., Papkov S.P., By the estimation of the stiffness of the macromolecules in solution polyamidbenzimidazole // Vysokomolekulyarnye Comm. Ser. B, 1983, 25, 7, 527-529 (in Rus.).

[15] IovlevaM.M., Physico-chemical aspects of the review of the role and mechanisms of action of lithium chloride in solution of fiber-forming polymers // Chem.fiber. 2001, 3, 10-13 (in Rus.).

Резюме

А. А. Талтенов, Г. Қ. Шамбилова

ПОЛИАМИДБЕНЗИМИДАЗОЛДЫҢ ДИМЕТИЛАЦЕТАМИДТЕГІ ЕРІТІНДІЛЕРІНІҢ ФАЗАЛЫҚ КҮЙЛЕРІ ЖӘНЕ РЕОЛОГИЯЛЫҚ ҚАСИЕТТЕРІ

Мақалада беріктілігі жоғары жылуға төзімді талшықтар мен күшейтілген пластиктерді алуға қолданылатын полиамидбензимидазолдың ерітінділері зерттелінді. Қатты тізбекті полимерлердің тұтқырлық қасиеттерінің фазалық ауысуларға өте сезімталдығы анықталды. Ол әсіресе сұйық кристалды фазаның түзілуі және полимерлер ерітінділерінің және қоспаларының аморфтық қабаттарға бөлінуі кезінде анық байқалады. 5%-дық ПАБИ реакциялық ерітіндісінің және полимердің ерегіштігін жақсарту үшін 3%-дық LiCl қосылған ПАБИ-дің полисульфонмен ДМАА-дағы қоспаларының реологиялық қасиеттері зерттелінді. Осы жүйеледегі қыздыру кезіндегі жүретін фазалық өзгерістерге байланысты болатын температуралық ауысулар анықталынды және сипатталынды. Фазалық диаграмманың концентрацияның зерттелген обылысына сәйкес бөлігі тұрғызылды. Вискозиметриялық және оптикалық әдістердің ПАБИ-ДМАА жүйесіндегі термодинамикалық ауысуларды дәл көрсететіндігі анықталды. Сонымен қатар ПАБИ-дің ПСФ-мен қоспасының ДМАА-тегі ерітінділерінің тұтқырлық қасиеттері әртүрлі температурада зерттелірді. ПАБИ-дің ДМАА-тегі ерітінділерінің зерттелген құрамдық диапазонының фазалық диаграмаларының төменгі критикалық араласу температурасының бар екендігімен сипатталады.

Түйін сөздер: полиамидбензимидазол, қатты тізбекті полимер, сұйық кристалдық фаза, диметилацетамид, фазалық диаграммалар, реологиялық қасиеттері, полимер ерітінділері, тұтқырлық.

Резюме

А. А. Талтенов, Г. К. Шамбилова

ФАЗОВОЕ СОСТОЯНИЕ И РЕОЛОГИЧЕСКИЕ СВОЙСТВА РАСТВОРОВ ПОЛИАМИДБЕНЗИМИДАЗОЛА В ДИМЕТИЛАЦЕТАМИДЕ

В статье исследованы растворы полиамидбензимидазола, применяемого для получения теплостойких высокопрочных волокон и армированных пластиков с использованием осадителей. Показано, что вязкостные свойства растворов жесткоцепных полимеров весьма чувствительны к фазовым переходам, что особенно ярко выражено при формировании ЖК-фазы или при аморфном расслоении растворов или смесей полимеров. Изучены реологические свойства 5%-ных реакционных растворов ПАБИ и смесей ПАБИ с полисульфоном в ДМАА с добавкой 3% LiCl, улучшающей растворимость полимера. Обнаружены и описаны температурные переходы в этих системах, связанные с фазовыми изменениями, происходящими в системе при ее нагревании. Построен участок фазовой диаграммы, отвечающей исследованной области концентраций. Показано, что вискозиметрический и оптический методы четко указывают на существование термодинамического перехода в системе ПАБИ–ДМАА. Также изучены вязкостные свойства растворов смесей ПАБИ с ПСФ в ДМАА при различных температурах. Фазовые диаграммы растворов ПАБИ в ДМАА в изученном диапазоне составов характеризуются наличием нижней критической температурой смешения.

Ключевые слова: полиамидбензимидазол, жесткоцепной полимер, жидкокристаллическая фаза, диметилацетамид, фазовые диаграммы, реологические свойства, растворы полимеров, вязкость.