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The rheological behavior of chemically crosslinked hydrogels based on poly(acrylamide)

Summary — The effects of different ratios of monomer/crosslinking agent and initiator/activator (potassium peroxydisulfate/ascorbic acid) concentrations on the polymerization of acrylamide (AAm) crosslinked with *N,N*-methylene-bis-acrylamide (Bis) were studied by dynamic oscilatory testing and gel point (*GP*) quantitative determination. In the studied conditions, rheological response of PAAm gelation — elastic and viscous moduli, loss tangent and complex dynamic viscosity — indicates these properties could transit between elasticity and viscoelasticity dependently on the reaction time and reactants' ratios. After a certain induction period during which the elastic modulus is close to zero, it increases monotonically until equilibrium is reached.

Key words: hydrogel, poly(acrylamide), redox initiation, viscoelastic properties, gel point, dynamic oscillatory method, *in situ* testing.

WŁAŚCIWOŚCI REOLOGICZNE CHEMICZNIE USIECIOWANYCH HYDROŻELI NA PODSTAWIE POLI(AKRYLOAMIDU)

Streszczenie — Metodą reometrycznych badań *in situ* scharakteryzowano właściwości lepkosprężyste w obszarze przemiany żelowania hydrożeli na podstawie poli(akryloamidu) (PAAm) sieciowanych *N,N*-metyleno-bis-akryloamidem (Bis) w roztworze wodnym układem redoksy nadtlenodisiarczan potasu (KPS, inicjator)—kwas askorbinowy (AAsc, aktywator). Określono wpływ stosunków masowych monomer/związek sieciujący (w przedziale od 0,01/0,99 % mas. do 99,67/0,33 % mas.) oraz KPS/AAsc (tabele 1 i 2) na wartości modułów sprężystości (G′) i stratności (*G*″), kompleksowej lepkości dynamicznej (η*), tangensa kąta stratności (tan δ) a także czasu żelowania (*GP*) (tabela 3, rys. 1—3); badania reometryczne prowadzono w stałych warunkach: (temp. 22 ^{o}C, ω = 0,1 Hz, s = 0,1 MPa). Ustalono, że badana charakterystyka reologiczna hydrożeli zmienia się w zależności od stopnia usieciowania (czasu pomiaru w trakcie żelowania *in situ*) od sprężystej do lepkosprężystej. Określono optymalne warunki żelowania z punktu widzenia końcowego zastosowania hydrożelu.

Słowa kluczowe: hydrożel, poli(akryloamid), inicjowanie redoksy, właściwości lepkosprężyste, punkt żelowania, dynamiczna metoda oscylacyjna, badania *in situ*.

POLYMER GELS AND HYDROGELS — GENERAL DESCRIPTION

Hydrogels are three-dimensional crosslinked or entangled polymer networks of both fundamental and technological interest. In these products individual hydrophilic polymer chains are connected — either by physical reversible intermolecular associations (van der Waals, electrostatic, hydrogen bonding) or by chemical covalent bonds. In contact with water this kind of structure is able to absorb a considerable amount of water without dissolving, showing the mechanical properties of solids and the diffusive transport properties of liquids. Due to high water content, hydrogels are used as biomaterials that can be in contact with tissues or biological fluids. For this reason, hydrogels have been extensively studied for biomedical applications, such as implants, soft contact lenses, and drug-delivery systems [1—4].

The kinetic of crosslinking reaction is an attractive area for a large number of investigations aimed at explanation of behavior and mechanism of macroscopic gelation, allowing *e.g.* controlling the production process and final performance of the systems. Dynamic rheology is a powerful tool to monitor crosslinking and microstructural changes in a material, as it allows the properties to be tested in *at-rest* conditions without disruption of the microstructure.

The viscoelastic behavior of polymer gels near the sol-gel transition has been studied experimentally and theoretically [3—11]. The main emphasis of these studies was to find the relation between linear viscoelastic properties and the structure of gel at the gel point. The experimental determination and prediction of gelation are important for the processing of crosslinking polymers, whereas the importance of the phenomenon and the universality of hydrogels properties make gelation interesting from a fundamental point of view.

The formation of polymer gel can be monitored from the time of evolution of viscoelastic material functions at the gel point (*GP*), where the entire network process can be divided into two parts separated by the gel point. The gel point is usually defined as the degree (or time) of reaction at which the solution no longer remains a liquid. Originally qualitative rheological considerations were used to define *GP*, what often was determined visually when no flow of the system was observed upon tilting it.

Winter and Chambon demonstrated, using end-linked poly(dimethylsiloxane) (PDMS) chemical gels formed *in situ* (*i.e.*, in the rheometer), that *GP* can be precisely identified and located by monitoring of the dynamic viscoelastic parameters throughout the reticulation process [5, 7]. In their investigations from 1986 on PDMS they observed a rapid increase in storage modulus and loss modulus with the decrease in loss tangent near the gel point during dynamic flow measurements [7]. These authors associated *GP* with the point where both oscillatory moduli have the same variations with the frequency.

Polymeric hydrogels derived from poly(acrylamide) (PAAm), crosslinked with a small amount of *N,N'*-methylene-bis-acrylamide (Bis) have found wide applications in the fields of agriculture and medicine as smart polymers. These applications include immobilization of biocatalysts, drug delivery systems, bioseparators, and protein adsorption [9, 10]. Since PAAm provides good networks, it was proposed as elastic model system in many physical investigations [12—15], being used to characterize hydrogel structure based on rheological measurements.

The network formation and structure of PAAm gel depend on many factors such as crosslinking density and distribution, chemical structure of crosslinking agent, various defects of the network, and parameters of the macrostructure (porosity, pore distribution by sizes, crystallinity, water in the system, *etc.*) [16, 17].

To gain a better understanding of the hydrogel viscoelasticity phenomenon near the sol-gel transition in relation to its final application, the rheology of *in situ* crosslinked poly(acrylamide) hydrogel synthesis by us and the results obtained are presented in this paper. The tests covered the viscoelastic properties (elastic storage modulus, *G'*, viscous loss modulus, *G''*, complex dynamic viscosity, η^*, and loss tangent, tan δ), during gelation process in isothermal conditions; they covered also the impact on the dynamic of these systems, by use of different monomer/crosslinking agent ratios and initiator/activator concentrations. The gel point was quantitatively determined using the stress-controlled oscillatory technique.

EXPERIMENTAL

Materials

Gels were prepared by crosslinking copolymerization of acrylamide (AAm) (Merck, Darmstadt, Germany) as the monomer with *N,N'*-methylene-bis-acrylamide (Bis) (Sigma, St. Louis, US) as crosslinking agent in aqueous solution at 6 % concentration. Potassium peroxydisulfate (Merck, Darmstadt, Germany) (KPS—initiator)/ascorbic acid (Sigma, St. Louis, US) (AAsc-activator) redox system was used to initiate the polymerization at ambient temperature (22 °C).

Sample preparation

There were performed two sets of experiments. In the first set, the monomer/crosslinking agent wt. % ratio had different values specified in Table 1. The reaction mixture was prepared from stock solutions of AAm (30 % w/v) and Bis (2 % w/v), by dissolution AAm and Bis in distilled water under constant stirring. Then, KPS (aqueous solution 1 % w/v) was added, followed by the addition of AAsc (aqueous solution 1 % w/v), (constant initiator/activator ratio = 0.1/0.01). In the second set of experiments, the samples 4.1—4.6 with the constant AAm/Bis wt. % ratio (see sample 4 in Table 1) were synthesized in the presence of KPS/AAsc at different wt. % ratios, as it is presented in Table 2. This sample preparation was done just before the rheological measurements to avoid early gelation.

Table 1. Syntheses of PAAm hydrogels — first set of experiments

Sample	AAm/Bis, wt. %	KPS/AAsc, wt. %[*)]
1	99.01/0.99	0.1/0.01
2	99.34/0.66	0.1/0.01
3	99.50/0.50	0.1/0.01
4	99.67/0.33	0.1/0.01

[*)] Calculated for 100 g of hydrogel.

Table 2. Syntheses of PAAm hydrogels — second set of experiments

Sample	AAm/Bis, wt. %	KPS/AAsc, wt. %[*)]
4.1	99.67/0.33	0.01/0.1
4.2	99.67/0.33	0.1/0.1
4.3	99.67/0.33	0.2/0.2
4.4	99.67/0.33	0.1/0.01
4.5	99.67/0.33	0.05/0.05
4.6	99.67/0.33	0.15/0.15

[*)] Calculated for 100 g of hydrogel.

In situ rheological testing

Reproducible rheological data for hydrogels below 10 % standard error is difficult to obtain because of hydrogel degradation by hydrolysis of the amide group or by swelling/deswelling process before the rheological test [18, 19]. Described below *in situ* monitoring minimizes this error sources — the values were obtained for freshly prepared solutions, during the gelation process.

2 ml of mixture of the previously mentioned reactants solutions were quickly poured on the lower plate of Bohlin CVO rheometer equipped with a Peltier device for temperature control, for each determination. The measurements were performed by using parallel-plate geometry. Both plates are made of stainless steel, with a gap of 500 μm, the upper plate having the radius of 30 mm.

The hydrogels were prepared *in situ* at 22 ± 0.1 °C for small amplitude rheological tests at a frequency (ω) of 0.1 Hz and shear stress (σ) of 0.1 Pa, within the linear viscoelastic range of oscillatory deformation. The macrostructure of the obtained hydrogel was not damaged after the different rheological tests.

RESULTS AND DISCUSSION

Influence of monomer/crosslinking agent (samples 1—4)

Figures 1 a—d illustrate the rheological response of PAAm gelation — *G′* (a), *G″* (b), tan δ (c) and η* (d) — recorded for different AAm/Bis ratios at constant temp. of 22 °C. The values of weight participation of Bis (Table 1) were ranging from 0.99 to 0.33 wt. %. The results indicate the rheological properties could transit between elasticity and viscoelasticity depending on time of reaction and composition.

From the evolution of *G′* value it is observed that the gelation process has an initiation phase when *G′* is close to zero, then sol-gel transition phase with the great increase in *G′* and finally the plateau regime with slight increase in *G′* until the equilibrium is reached (Fig. 1 a).

At low Bis content (sample 4 in Table 1), the viscous loss modulus exhibits a behavior similar to *G′* (Fig. 1b). For this sample, the final value of *G″* is about 7 Pa, which is about 10 times smaller than the elastic modulus. For higher Bis contents, *G″* oscillates near zero at the beginning of the polymerization, then stabilizes to a constant value. The polymerization is completed when *G′* and *G″* reach plateau values with reaction time and tan δ is lower than 1 (Fig. 1c). The decrease in loss tangent is interpreted as an increase in the elastic character of the material as a three-dimensional network structure develops.

In all cases, these samples were initially low-viscosity liquids (Fig. 1d) and displayed almost no elastic response; η* shows a gradual increase in the formation of hydrogel with an elastic modulus *G′* with time. *G′*, as it was said, increases also with time.

Influence of initiator/accelerator concentration and ratio (samples 4.1—4.6)

Usually, the crosslinking copolymerization of AAm with Bis is initiated by ammonium peroxydisulfate as radical initiator and with *N,N,N′,N′*-tetramethylethylenediamine as accelerator. This reaction is inhibited by atmospheric oxygen. As a consequence, the reaction medium must be degassed and nitrogen drived before starting the reaction.

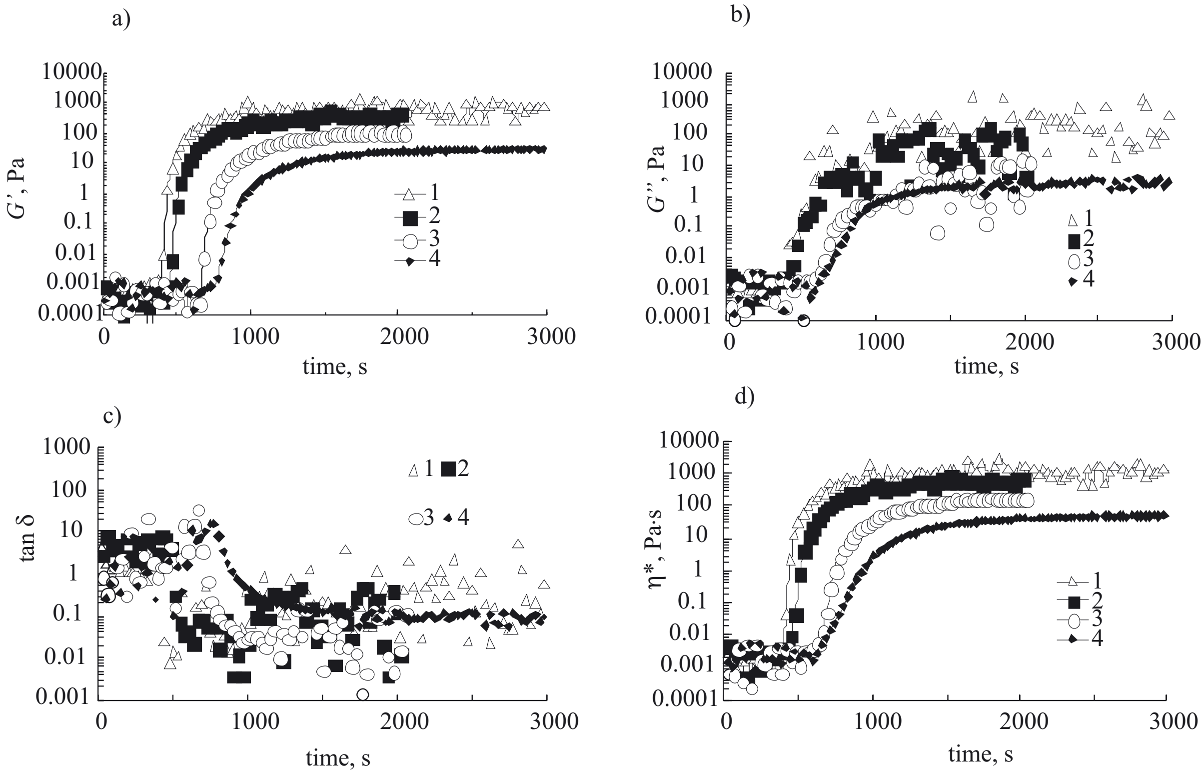
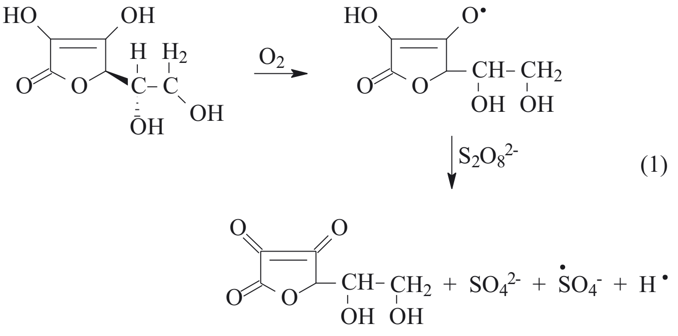


Fig. 1. Changes of (a) G′, (b) G″, (c) tan δ and (d) η as functions of AAm/Bis wt. % (samples 1—4 in Table 1); all experiments were performed at 22 °C, σ = 0.1 Pa and ω = 0.1 Hz*



(1)

In our study, in case of redox system potassium peroxydisulfate/ascorbic acid initiating the reaction, the presence of molecular oxygen instead of inhibiting, autocatalyzes the polymerization [20, 21].

The concentrations and ratios of two components of redox initiation system used in this study have influence on the rheological behavior of the system during gelation. The effects are evident on elastic and viscous moduli, loss tangent and complex viscosity, but on the gel point, too. Crosslinking reactions are able to connect macromolecules into a tridimensional polymeric network. The system reaches its *GP* at a critical extent of reaction, when it loses its solubility, the steady-shear viscosity diverges to infinity, and the equilibrium modulus starts to rise to a finite value [3].

The elastic modulus (*G*)', viscous modulus (G'') and loss tangent (tan δ) for the samples 4.1—4.6 from Table 2 are presented in Figures 2 a—f.

Beyond *GP*, the network stiffness continues to increase steadily with crosslinking degree increase until

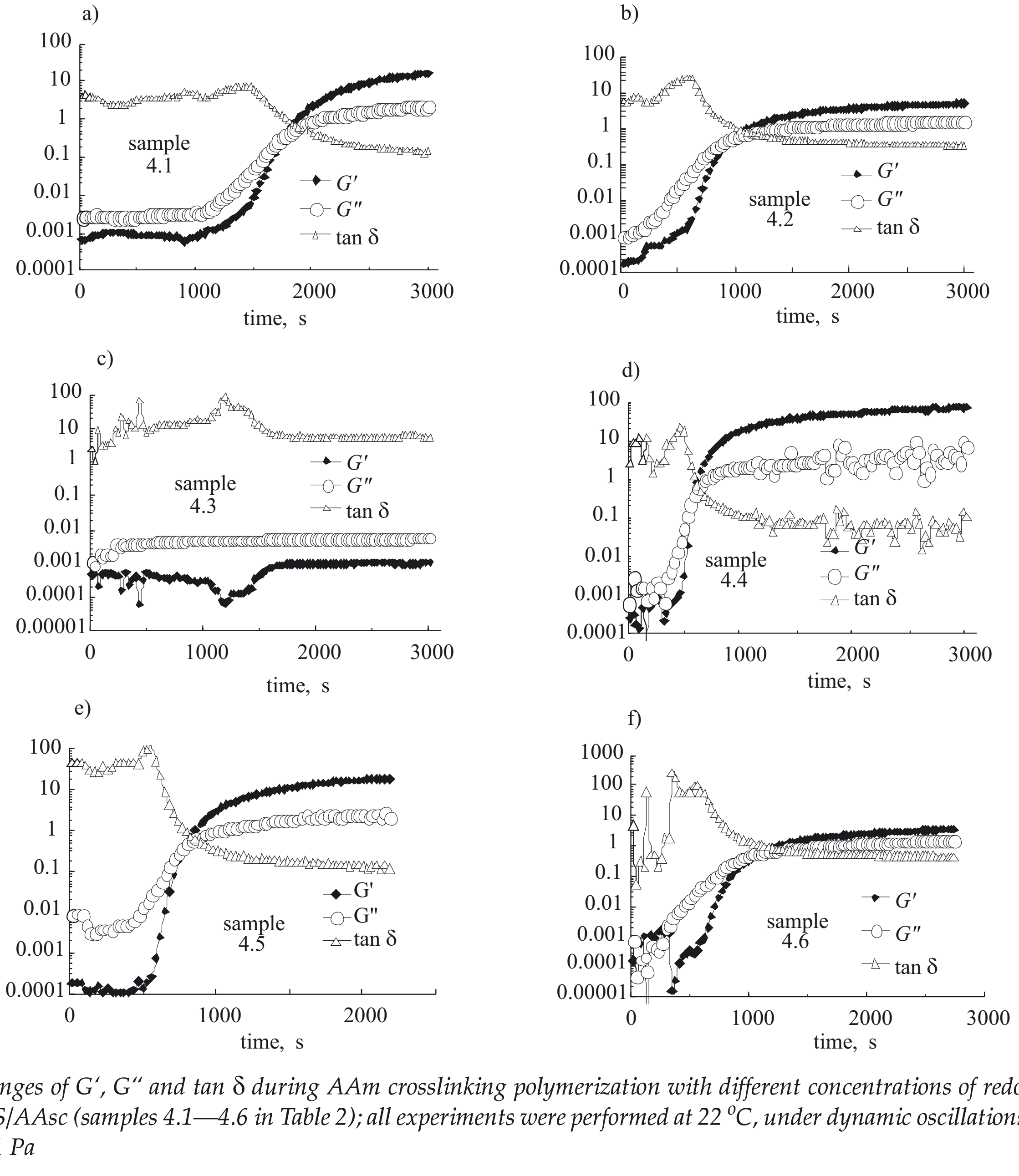


Fig. 2. Changes of G', G'' and tan δ during AAm crosslinking polymerization with different concentrations of redox initiation system KPS/AAsc (samples 4.1—4.6 in Table 2); all experiments were performed at 22 ^{o}C, under dynamic oscillations, at ω = 0.1 Hz, σ = 0.1 Pa

the system reaches completion of the chemical reaction. For all the variants of hydrogel syntheses, the viscous behavior of the oligomeric material dominates the initial part of the experiment. The viscous modulus, *G"*, is greater while the elastic modulus, *G'*, is still negligible. With the crosslinking polymerization advances, *G"* keeps increasing with the same rate, while *G'* rises sharply until it intersects and then exceeds the viscous modulus. Both moduli level off as the reaction comes to completion. This aspect of *G'* and *G"* representations is not met for the sample 4.3 (Fig. 2c) where no gelation appeared in the specified conditions of reaction.

According to the Winter—Chambon criterion [7] *GP* is located at the intersection between the elastic (storage) modulus and the viscous (loss) modulus, measured in oscillatory viscometric motions with low strain amplitude, constant applied shear stress amplitude, and constant frequency (ω). In our previous study [21] we found that Winter—Chambon criterion was valid for the system investigated in this paper. After the gelation point, *G'* exceeded *G"* as the network developed and tended to attain a plateau.

The gelation process is sometimes described by the time evolution of the loss tangent $\tan \delta = G''/G'$, where $\tan \delta \to \infty$ at the onset of the process (fluid behavior) and $\tan \delta \to 0$ when the reaction is completed; the loss tangent reaches the value 1 at the intersection where $G' = G''$. Thus, in all studied cases, except of sample 4.3 with no gelation, beyond the gel point $\tan \delta > 1$ and decreased monotonically (Fig. 2) as the samples became significantly more elastic. Likewise, the initial increase in tan δ with time implies an initial period during which the viscous modulus increases more rapidly than the elastic one.

Therefore, the representations in Fig. 2 are used to calculate G''_∞/G'_∞ and *GP* for the samples 4.1—4.6 (Table 3). Supplementary, this behavior is underlined by the complex viscosity, η*, plotted in Fig. 3 for some selected KPS/AAsc initiation system wt. % ratios.

Table 3. Viscoelastic behavior during PAAm hydrogels syntheses

Sample	KPS/AAsc, wt. %[*)]	G''_∞/G'_∞, %	*GP*, s
4.1	0.01/0.1	13.75	1773
4.2	0.1/0.1	32.64	987
4.3	0.2/0.2	No gelation	No gelation
4.4	0.1/0.01	3.797	610
4.5	0.05/0.05	13.12	774
4.6	0.15/0.15	44.71	1075

[*)] Calculated for 100 g of hydrogel.

Figure 3 shows the dependence of complex viscosity on the reaction time. The results are consistent with the previous ones; at the beginning of curves η* increases gradually, reflecting the balance between viscous and elastic behavior of the reaction system during gelation. In this initial stage the viscous behavior is dominant till the gelation appeared; after the gel point, elastic behavior is dominant. Completed reaction and stable final hydrogel structure is represented by the plateau value.

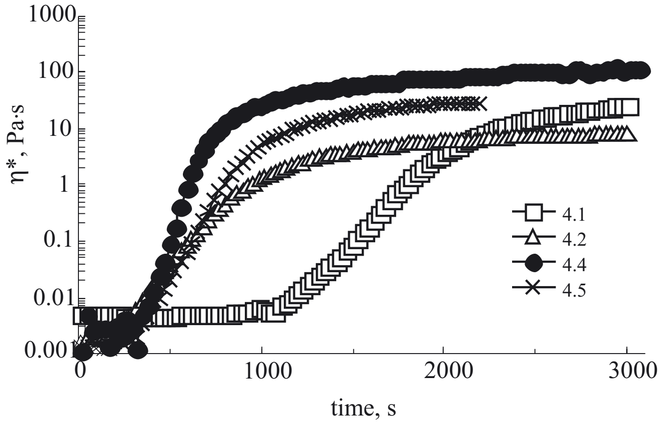


Fig. 3. Changes of the complex viscosity (η) of some of 4.1—4.6 samples during the syntheses of PAAm hydrogels at 22 °C, under dynamic oscillations at ω = 0.1 Hz, σ = 0.1 Pa*

Sample 4.4 synthesized at a wt. % ratio of AAm/Bis of 99.67/0.33 and KPS/AAsc wt. % of 0.1/0.01 has optimum cumulative viscoelastic properties (elastic/viscous behavior, gel point, viscosity) in relation to the subsequent application followed by this research.

CONCLUSIONS

We applied the rheological monitoring during polyacrylamide hydrogel synthesis as a powerful tool in determination of the best parameters of synthesis, leading to the optimum structure properties balance.

The influence of wt. % ratio of AAm/Bis and KPS/AAsc wt. % ratio during the crosslinking polymerization of AAm was *in situ* studied under dynamic oscillations at constant shear stress of 0.1 Pa, frequency of 0.1 Hz and at temperature 22 °C.

By modulation the monomer/crosslinking agent ratio, the variant of synthesis with 99.67/0.33 AAm/Bis wt. % ratio is established as the optimum variant of this reaction from the point of view of viscous/elastic behavior and viscosity. According to this variant, KPS/AAsc 0.1/0.01 wt. % ratio leads to $G''_\infty/G'_\infty = 3.797$ and *GP* = 10 s, *i.e.* optimum product from the point of view of final application of hydrogel.

ACKNOWLEDGMENTS

The study was supported by the Project No. 466/22.01.2009, entitled "Researches in the field of polymeric matrices design for sensitive structures" of the IDEI PROGRAM.

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Received 29 XI 2008.