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Managing of hydrogen bonding in aqueous poly(vinyl alcohol) solutions: new perspectives towards preparation of more homogeneous poly(vinyl butyral)

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Abstract

This paper follows up investigations in the field of solution properties of poly(vinyl alcohol). Here we present a combined investigation based on both theoretical and various experimental methods focused on peculiarities in hydrogen bond reorganization in aqueous poly(vinyl alcohol) solutions discussed as a function of temperature. It was demonstrated that the specific polymeric effect takes place in binary poly(vinyl alcohol)/water systems. The effect is characterized by the delay in response of the polymer system on heating until the critical temperature is reached. It was demonstrated in this paper that hydrogen bond reorganization in binary aqueous systems may lead to an increase in the degree of undesirable intermolecular cross-linking reaction. This finding was in contrast to previously made proposition based on hydrogen bond reorganization in ternary poly(vinyl alcohol) solutions. This assumption based on the theoretical studies was confirmed experimentally. Thus, a series of poly(vinyl butyral) samples were synthesized in various solvents using traditional catalysts (HCl) as well as the modern thermosensitive polymeric catalyst. It was demonstrated by using GPC and viscometry experiments that poly(vinyl butyral) samples with a low degree of acetalization (<10%) prepared in water in the absence of co-solvent additives are characterized by large molecular weights and bimodal molecular weight distribution. On the contrary, polymers prepared in mixed (ternary) systems and in the presence of a thermosensitive polymeric catalyst demonstrate relatively narrow molecular weight distribution. This indicates the preparation of more homogeneous products which also facilitates mechanisms of hydrogen bond reorganizations observed in binary and ternary poly(vinyl alcohol) solutions.

Keywords Hydrogen bond · Poly(vinyl alcohol) · Poly(vinyl butyral) · Polymer coil · Polymeric catalyst · Langevin dynamics

Introduction

Poly(vinyl butyral) (PVB) is one of the most important industrial products demanded all over the world. This polymer is characterized by a unique set of adhesive and binding properties, high strength of fibers and film materials, thanks to which PVB finds wide application in civil and military industries. In particular, plasticized PVB is used as a laminating film in the production of safety glasses (triplex), and is also used as an adhesive in the production of varnishes, primers, enamels and mastics.

In general, PVB with different content of acetal groups is obtained in water by condensation reaction between two OH-groups of PVA and butyraldehyde in presence of an acid catalyst. PVA/water systems used in PVB manufacture are prone to structuring with consecutive formation of strong interchain interactions. This in turn causes side reactions that reduce the quality of the final products. Among them are undesirable intra- and intermolecular cross-linking (non-cyclic or linear acetal formation instead of 1,3-dioxane ring) [1, 2]. The intermolecular cross-linking leads to an increase in the heterogeneity of the synthesized PVB thus decreasing the quality of the product due to the deterioration of PVB performance properties. Among other things, the solubility of PVB in certain

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solvents is decreased, which makes it difficult to obtain valuable technical products based on cross-linked PVB. The ratio of intra- and inerchain cross-links may depend on the synthesis conditions such as initial PVA concentration, type of the used solvent, temperature of the reaction, etc. It was also assumed that the cross-linking reaction can be controlled thermodynamically through the selection of the appropriate conditions [2–4]. Intuitively one can state that in a dilute regime, even in a good solvent, the PVA molecules adopt the conformations of dense coils and intramolecular cross-linking takes place [2]. In concentrated solutions, a new phenomenon called chain entanglement arises [5], and intermolecular cross-linking prevails. In line first proposition it was previously shown that the anomalous retardation of the acetalyzation of PVA with butyraldehyde was observed in dilute polymer solutions (1 wt.%) using kinetic experiments, as well as rheological studies [6]. The retardation effect thus revealed was explained in terms of the conformation of the polymer chains and possible intramolecular crosslinking. Among the works of this series, one can mention the work of Gebber et al. [2] In this article, the crosslinking reaction of PVA in dilute solutions was studied using viscometry and GPC methods. It was demonstrated that intramolecularly (within a single coil) cross-linked PVA chains adopt more dense conformations compared to isolated but not cross-linked chains. It was also established that the size of macromolecules decreases with an increase in the degree of cross-linking.

NMR, viscometric and refractometric methods were applied in another work in order to study comparisons in thermodynamics between poly(vinyl alcohol)/water/co-solvent ternary solutions with group of organic co-solvents [4]. Experiments revealed that hydrogen bonds between 1,4-butanediol and 2,4-pentanediol (poly(vinyl alcohol) model) molecules are stronger than the hydrogen bonds formed between 2,4-pentanediol and other considered solvents. From rheological and viscometric experiments, it was established that ternary solutions of poly(vinyl alcohol) with 1,4-butanediol as co-solvent show an essential increase in the values of reduced viscosity above 35 °C thus revealing the critical temperature phenomenon which is unique for the solutions of strongly associated polymers. It was proposed that the described type of organization in presence of co-solvent additives may lead to the decrease in the degree of intermolecular cross-linking.

The goal of current research was to study peculiarities in hydrogen bond reorganization in aqueous PVA solutions with change in temperature and PVA concentration using both experimental techniques and computer modeling and thus to complement the results of our previous investigations [4] demonstrating the relationship between the conditions of the acetalization reaction and the characteristics of the obtained products. The first part of the paper is dedicated to the study of peculiarities in hydrogen bonding observed in PVA/water

solutions using Langevin dynamics and viscometry experiments while the second part is attributed to the differences in characteristics of PVB samples synthesized in solvents with different thermodynamic quality with respect to PVA.

Experimental

Materials

Commercial PVA with an average polymerization degree of 1130 and saponification degree above 99%, butyraldehyde >98% GC (Sigma) were used without further purification. Commercial DMSO and 1,4-butanediol were purified by recrystallization and dried over activated molecular sieves (4 Å) before use. Tetrahydrofuran (THF) was dried over potassium hydroxide and distilled in presence of potassium hydroxide prior to use.

Methods

PVA solutions in the range 2–10 wt% were gravimetrically prepared by dissolving PVA in an appropriate solvent at 80–90 °C. Less concentrated solutions were prepared from a 2 wt% stock solution by dilution. The prepared solutions were gently filtered through a synthetic filter, and their viscosities were measured with falling ball (Höppler B3) or rotational (Brookfield LVT) viscometers.

^{1}H NMR spectra were obtained at 400 MHz using an Agilent DD2 400 spectrometer and were recorded in dmso-d6 with tetramethylsilane (TMS) as the internal standard. All ^{1}H NMR measurements were carried out at 25 °C.

Purity of the starting chemicals and butyraldehyde consumption in a course of acetalization were determined via gas chromatography using a Chromos GC-1000 chromatograph equipped either with a VertiBond AqWAX capillary column (length 60 m, I.D. 0.32 mm, film 0.50 mm) or ValcoBond VB-1 capillary column (length 60 m, I.D. 0.32 mm, film 0.50 mm) and flame ionization detector. The temperature of the flame ionization detector and sample injector was set to 250 °C.

Gel permeation chromatography (GPC) was performed on a Chromos LC-301 equipped with isocratic HPLC pump Lab Alliance Series 111 and differential refractometer detector Waters 410. Ultrahydrogel 250 (pore size 250 Å, molecular weight range: 1 K - 80 K) and Ultrahydrogel 1000 (pore size 1000 Å, molecular weight range: 2 K – 4 M) were used as GPC columns to measure the molecular weights of the synthesized polymers. Linear polyethylene oxide (PEO) standards with molecular weights equal to 25,300, 44,000, 78,300, 152,000, 326,000, 558,000 and 810,000 Da were used for the calibration. To obtain the calibration coefficients, the values of the Mark-Houvink coefficients was used [7]: PEO:

$\kappa = 3.47 \times 10^{-4}$, $\alpha = 0.7$; ПВС, PVB: $\kappa = 1.332 \times 10^{-3}$, $\alpha = 0.57$. Temperatures of thermostat and detector were set to 35 °C and 30 °C respectively. Water solution of sodium nitrate (0.1 M) with a flow rate equal to 0.7 ml/min was used as eluent. PVA samples were dissolved at 80–90 °C, after which the resulting solution was heated for 1 h at 90 °C prior to filtration. PVB samples were dissolved at ambient temperature. The preheated solution was filtered through a "millipor" membrane filter with a pore size of 0.45 μm.

Dynamic laser light scattering (DLS) measurements were performed on a Photocor Complex spectrometer at the wavelength equal to 659.016 nm. Temperature deviations were maintained within 0.01 °C. The correlation functions were recorded at a scattering angle of 90°. Cycle protocol was used to gain the scattering data. The duration of each time unit was set to be either 10 or 5 s. The number of units was equal to 60 and thus the total duration of run at definite temperature was equal to 600 and 300 s depending on the duration of each time unit. The number of runs was set to at least 2. The base line shift and spike tolerance were set to be 0.005 and 30% correspondingly. Percentage of the correct units was found to be no less than 80% for each of the cases. Time correlation functions were analyzed with integrated DynaLS soft. Particles distribution analysis was performed with number of intervals equal to 200 to treat the obtained scattering data. Prepared polymer solutions were filtered using PET filters (polyester, 0.2 mm, d = 13 mm) prior to the measurements.

Polymer synthesis

Synthesis of polymeric catalyst poly(N-(tert-octyl)acrylamide-co-2-acrylamido-5-(trifluoromethyl)pyridine) (Copolymer **1**) was analogues to the one described previously [8].

Procedure for the preparation of PVB with different degree of acetalization was also described in our previous papers [6, 9].

Langevin dynamics simulations

Langevin dynamics (LD) was used to study the structural features of polymer coils. The model of the atactic PVA chain was constructed using the Avogadro program. Preliminary optimization was performed using MMFFaq force field (Avogadro). In this study the atomistic model of PVA with number of elementary units (polymerization degree) $n = 90$ was used. The ratio of iso−/syndio−/heterotactic triads within the model was set to be 0.22/0.29/0.49, which corresponds to the experimental data obtained in the course of investigation of microstructure of a commercial PVA sample using ^{13}C NMR.

Conformation of a single PVA coil obtained in the course of the study of folding of PVA chain was used as initial conformation to study the thermodynamics features of interaction between two PVA coils. Geometry of the single coil was

optimized using MMFF94 force field prior to the LD simulations. AMBER99 was used as a force field in a course of LD simulations. Lenard-Jones 10–12 potential was used to account for the hydrogen bond interactions. The potential energy of the system comprises the energy of electrostatic interactions (the Coulomb part of the potential energy). The latter usually (for standard force fields) defines as:

$$Uc = \Sigma q_i q_j / \varepsilon_0 R_{ij} \tag{1}$$

where qi and qj are the point charges assigned to atoms i and j, Rij is the distance between atoms i and j, and ε_0 is the dielectric constant of vacuum or another medium.

In the absence of solvent molecules given explicitly, the Coulomb part of the potential energy is large and makes a significant contribution to the total energy, even at considerable molecular distances (unlike, for example, van der Waals interactions, the energy of which is inversely proportional to Rij^6 – i.e. strongly decreases with an increase in distance between the interacting centers). Thus, for unit charges at a distance of 20 Å, the contribution of Coulomb interactions to the total energy is ~ 17 kcal/mol. In this work, a method in which the dielectric constant depends on the distance between two point charges (distance dependent dielectric constant) was used to simulate the solvent molecules (water) implicitly. Thus, the expression for the Coulomb energy is modified and takes the following form:

$$Uc = \Sigma q_i q_j / D\varepsilon_0 R^2_{ij} \tag{2}$$

In this case, unlike expression (1), the energy is inversely proportional to R^2. This approximation makes it possible to imitate to some extent the screening effect of water. Therefore, the contribution of electrostatic interactions is markedly leveled, for atoms at a distance of 6–8 Å. The interaction of PVA chains with a solvent (water) was also specified implicitly through the friction coefficient. The friction coefficient, γ, ps^{-1} of water was calculated using following equation:

$$\gamma = 6\pi\eta/m, \tag{3}$$

where m is the mass of the particle; η is the viscosity of the solvent.

Under real conditions, a change in temperature leads to a change in the viscosity of the solvent, which, according to Eq. (3), should also affect the friction coefficient. Therefore, the values of γ corresponding to a given temperature were determined to accounts for the decrease in viscosity of aqueous solution with an increase in temperature (Fig. 1).

The simulations were carried out at constant temperatures ranging from 283 to 373 K (10 K step) for each pair of PVA
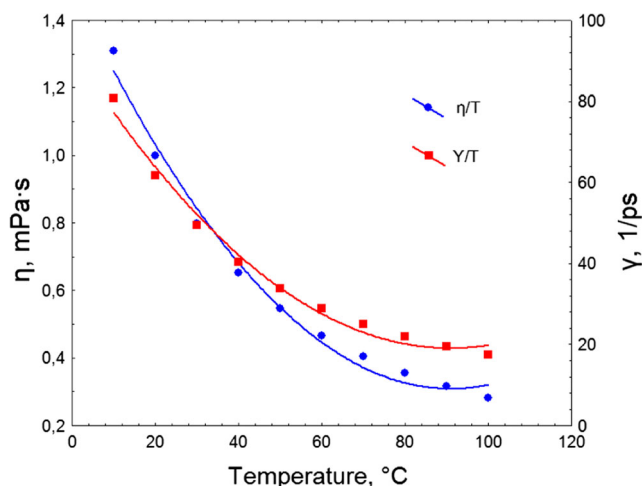
Fig. 1 Viscosity (η) and friction coefficient (γ) as a function of temperature for water calculated using Eq. (3)

coils possessing identical initial geometry. To control the temperature, the Berendsen thermostat [10, 11] was used, with relaxation time equal to 0.1 ps [11–13]. The initial rates for equilibration were set randomly in accordance with Maxwell-Boltsmann distribution of speeds. Velocities on atoms obtained in a course of equilibration period were used for the accumulation of the final trajectories. The equilibration time was set to 200 ps for thermodynamic calculations (2 interacting coils) and 100 ps for isolated (single) coils. To integrate the Langevin equation, the Allen and Tildesley method [14] was used with a time step of 1 fs [10, 11]. For the interaction of two PVA macromolecules, the simulation time was equal to 4 ns and the atomic coordinates and velocities on atoms were saved every 5 fs. For individual PVA chains with different initial conformation the simulation time varied from 4 to 8 ns. Energetically most stable conformations were selected from the last 100 ps of simulation for the subsequent analysis.

The density of hydrogen bonds (D_{HB}) between OH-groups of interacting coils, as well as the total density of hydrogen bonds within the given molecular system, was calculated to study the dynamics of the structure parameters of the PVA-based systems. In general, the density of hydrogen bonds was determined as the ratio of the number of detected hydrogen bonds in the system (N_{HB}) to the total number of functional (OH) groups in the system capable of forming a hydrogen bond (ΣN_{HB}):

$$D_{HB} = \frac{N_{HB}}{\Sigma N_{HB}/2} \qquad (4)$$

The factor of 2 in the denominator indicates the formation of a single hydrogen bond between two OH groups. Thus, in the case of pairwise interactions realized between all of the OH-groups in the system D_{HB} adopts the value equal to one. The specified assumption of formation of a single hydrogen bond between two OH-groups is conditional, since in real polymer systems one can observe domains in which one OH-group adopts a favorable steric arrangement for the formation of two or more hydrogen bonds. With a sufficient number of such domains in the system, the value may exceed the value equal to one. Nevertheless, the applied approach is convenient since it allows one to compare the hydrogen bonding parameters for the systems of the same type (with equivalent type of hydrogen bond forming functional groups), but with different structure features of the comprising molecules (degree of polymerization, degree of substitution, presence of additional functional groups, etc.).

Results and discussion

Peculiarities in hydrogen bond reorganization in PVA systems. Conformation of isolated PVA chain

To study the geometry parameters typical for PVA macromolecules in dilute solution, the Langevin dynamics (LD) method was used. This method allows one to simulate the solute-solvent interactions in an implicit manner, through an adjustable parameter γ (the friction coefficient). This term is the hydrodynamic characteristic of a solution and depends on temperature. Simulation of the polymer–solvent interaction using LD approach is convenient and efficient when the interactions between solvent and polymer are thermodynamically less favorable in contrast to polymer–polymer interactions (the latter is more thermodynamically favorable). Previously published data based on the light scattering, as well as spectral measurements and quantum-chemical calculations [15–17] indicate that for PVA–water systems interactions between OH-groups of the polymer are more energetically favorable in contrast with interactions realized between OH-groups of PVA and water. These data specified that water is not a good solvent for PVA.

In the course of LD simulations, the values of the total energy associated with different geometries of the PVA chain were calculated. The obtained data indicate that in dilute solution, the single PVA chain tends to fold to adopt a conformation of a dense coil since the total energy of the system decreases from 1677 kcal/mol for the fully unwrapped chain to 1280 kcal/mol for the chain with the conformation of a dense coil. According to quantum-chemical calculations, the association between OH-groups of PVA is stronger than the association between OH-groups of PVA and water molecules [4, 6]. The described differences in strength of hydrogen bonds are responsible for the conformation of a dense coil adopted by the macromolecule characterized by the maximum possible number of hydrogen bonds within the coil. Stabilized by numerous hydrogen bonds, the compressed conformation is energetically more favorable under conditions when water

is used as a solvent. These observations are also confirmed by the experimental data described previously [4].

The situation changes with an increase in the volume fraction of coils in the mixture. Reaching a critical concentration, macromolecular coils begin to overlap. As a result, the polymer coil obtains another way to effectively reduce energy which is the formation of hydrogen bonds with OH-groups of other chains. Such interactions are equivalent to those realized within a single coil. As an example, Fig. 2 shows PVA coils before (A) and during interaction simulated via LD.

According to Anna Tager [18], the distance between chain ends characterizes the volume (or size) of a polymer coil. In practice, the root-mean-square distance between the chain ends$\langle r^2 \rangle$ is often used. Analysis of the obtained data allows us to conclude that the interaction of PVA coils and the formation of hydrogen bonds between them leads to the unfolding of the coils. It was found that $\langle r^2 \rangle$ for a single polymer coil increases from 224.4 Å^2 for the isolated (dilute regime) PVA coil to 400 Å^2 for the system consisting of two interacting coils. This effect is caused by the reorganization of part of the intramolecular hydrogen bonds formed within a single coil into intermolecular hydrogen bonds during interaction of two initially dense polymeric coils.

Effect of temperature on the structure and dynamics of interacting PVA coils. Polymeric "delay" effect

It was previously shown that the conformation of a polymer chain strongly depends on temperature. Heating should have a twofold impact on the polymer conformation. It should obtain a more compact one, because the expansion factor is decreased [19]. On the contrary, it should expand, because heating influences the decrease in the degree of association. The last statement is especially important for the systems with specific, strong interactions, such as H-bonding. Most of the previously described works on modeling PVA solutions is devoted to studying the interaction of macromolecules and oligomeric fragments of PVA chains with water molecules using isothermal molecular dynamics simulations. Nevertheless, one can find several works that study the effects of temperature on the characteristics of PVA in solutions. In one of such researches [11], PVA oligomers consisting of 30

elementary units are studied at temperatures of 293, 303, and 323 K under conditions of a dilute solution. The main conclusion made by the authors consists in the fact that for efficient simulation of PVA systems, it is necessary to apply models with a degree of polymerization of $n > 30$. The narrow temperature range, low molecular weights of oligomers, and the isolation of PVA chains in the studied systems do not allow one to answer the questions concerning the structural changes of the polymer chains under the conditions of semi-dilute solutions with pronounced intermolecular and intersegment interactions, as well as peculiarities in thermodynamics of such systems. There are literature examples on the thermodynamic analysis of PVA solutions using computer simulation, as well as the presence of significant experimental material on this topic. Even so, the effect of temperature on the behavior of PVA chains under conditions of interacted chains (semi-diluted mode) in a thermodynamically moderate good solvent remains unclear. For this reason, a theoretical study of the thermodynamics of systems containing PVA is the goal of this section.

Thus, the analysis of the dynamics of the structural factors was carried out to establish the mechanism of structural reorganization for the PVA-based systems. Figure 3 shows the dependence of the total density of hydrogen bonds ΣD_{HB} (all hydrogen bonds in the system are considered) on temperature. Meanwhile, Fig. 4 depicts three-dimensional surfaces representing D_{HB} and ΣD_{HB} as a function of temperature.

An interesting observation is a uniform decrease in the ΣD_{HB} parameter is not observed, as one could expect based on the sensitivity of associative interactions (in particular, hydrogen bonds) with respect to temperature. ΣDHB barely changes at the initial stage (below 330 K), as can be clearly seen observing surface in Fig. 4 (bright yellow plateau). This dependence is maintained until the system reaches T*, after which a sharp inflection in the region of brown spot occurs corresponding to the maximum density of all types of hydrogen bonds (ΣD_{HB}) formed in the studied system. With further rise in temperature, a wavy decrease in ΣD_{HB} and rise in D_{HB} (green area) parameters were observed. The minimum ΣD_{HB} value was found to be ~0.4 at temperatures in the range 360–370 K. The obtained data allowed one to establish the relationship between the decrease in the total density of hydrogen bonds in the systems and the

Fig. 2 Snapshots of PVA coils before (A) and in the course of LD simulation. The calculation was performed at 300 K
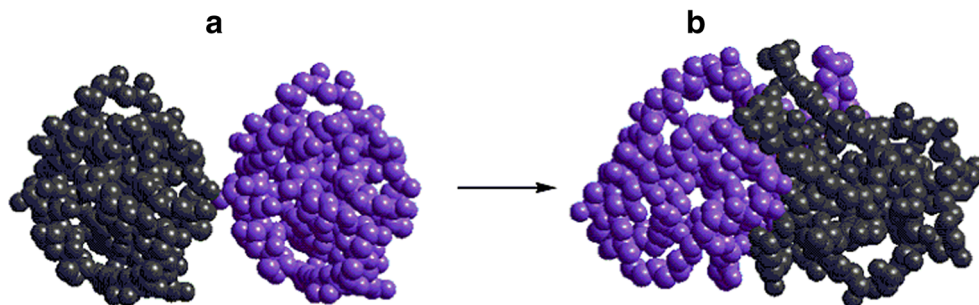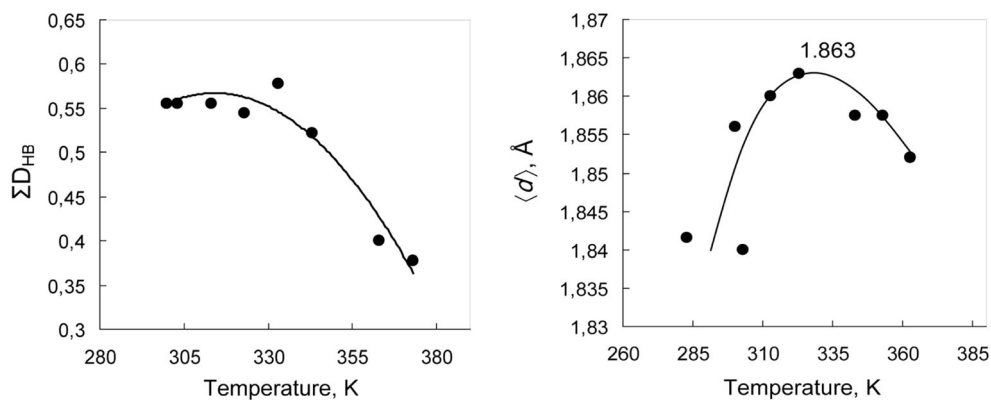
Fig. 3 Left: total density of hydrogen bonds (ΣD_{HB}) as a function of temperature for systems consisting of two interacted PVA coils. Right: temperature dependence of the average length of hydrogen bonds $\langle d \rangle$ formed between segments of PVA coils. The number shows the maximum value of $\langle d \rangle$ obtained in the course of calculations performed at 323 K

increase in the density of hydrogen bonds between the coils while reaching the critical temperature. Figure 3 (B) also shows the change in the average length of intersegment hydrogen bonds in PVA coils $\langle d \rangle$ as a function of temperature. This dependence supplements the data on the change in the total density of hydrogen bonds with an increase in temperature in the initial part of the temperature curve. As noted above (Figs. 3 and 4), a uniform decrease in ΣD_{HB} is not observed until the critical temperature is reached, which is not entirely in line with expectations based on the idea of the hydrogen bonds lability towards heating. New data as shown in Fig. 3 (B) indicate that with an increase in temperature, the value of the average length of intersegment hydrogen bonds increases to a certain limit with a maximum value of $\langle d \rangle$ equal to 1.863, recorded for the region of critical temperature. The increase in $\langle d \rangle$ indicates a weakening of hydrogen bonds in the system, which leads to their redistribution. At the same time, the permanence of ΣD_{HB} up to T* is associated with peculiarities of hydrogen bond organization within the studied polymeric system, which in turn strongly depends on the

hydrogen bond strength and quantity. Figure 5 shows a fragment of a PVA coil depicting several hydrogen bonds centered on one OH-group (one-center hydrogen bonds).

This picture is typical for the interacted coils when the system reaches a certain temperature. In contrast to PVA coils studied at lower temperatures, in which hydrogen bonds are distributed relatively evenly, macromolecular coils possessing the single-center domains demonstrate heterogeneity in hydrogen bond distribution. In such structures, one can find regions with a higher density of hydrogen bonds and regions depleted in hydrogen bonds. The mechanism of formation of the domains shown in Fig. 5 can be described as follows. As the temperature rises, hydrogen bonds become weaker. Hence, they are prone to break more easily, which in turn increases the local mobility of the segments within a given coil. However, the segments of the polymer chain do not have enough time to disperse under the influence of thermal motion due to the high density of the coil (compressed conformation) and
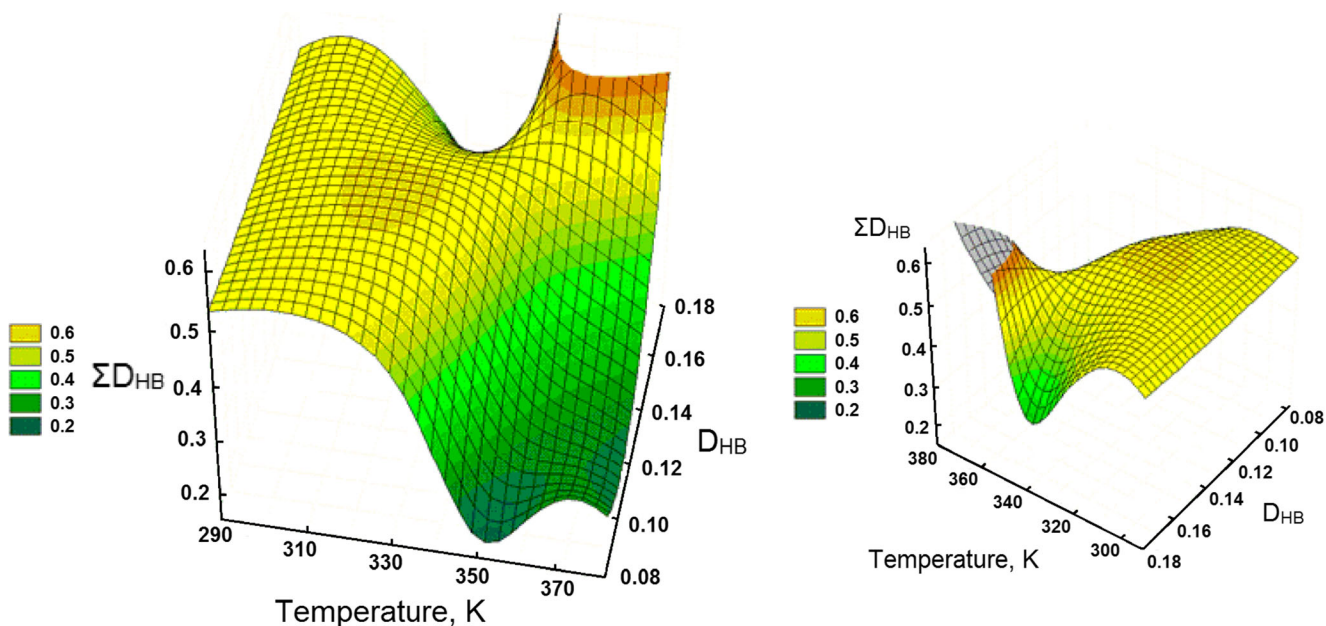
Fig. 4 Three-dimensional surface demonstrating D_{HB} and ΣD_{HB} as a function of temperature for the system with pair of interacted PVA coils

Fig. 5 Top: fragment of PVA coil illustrating the formation of a multi-linked OH-group. The geometry was obtained during LD simulation of the interaction between two PVA coils at 343 K. The figure also shows a part of PVA chain containing unbonded OH-groups (loop). Hydrogen bonds are shows by dashed lines. The length of one of the hydrogen bonds of the domain is underlined. Bottom: PVA coils with different degrees of deformation, extracted from the system of two interacting PVA coils simulated with LD method at different temperatures
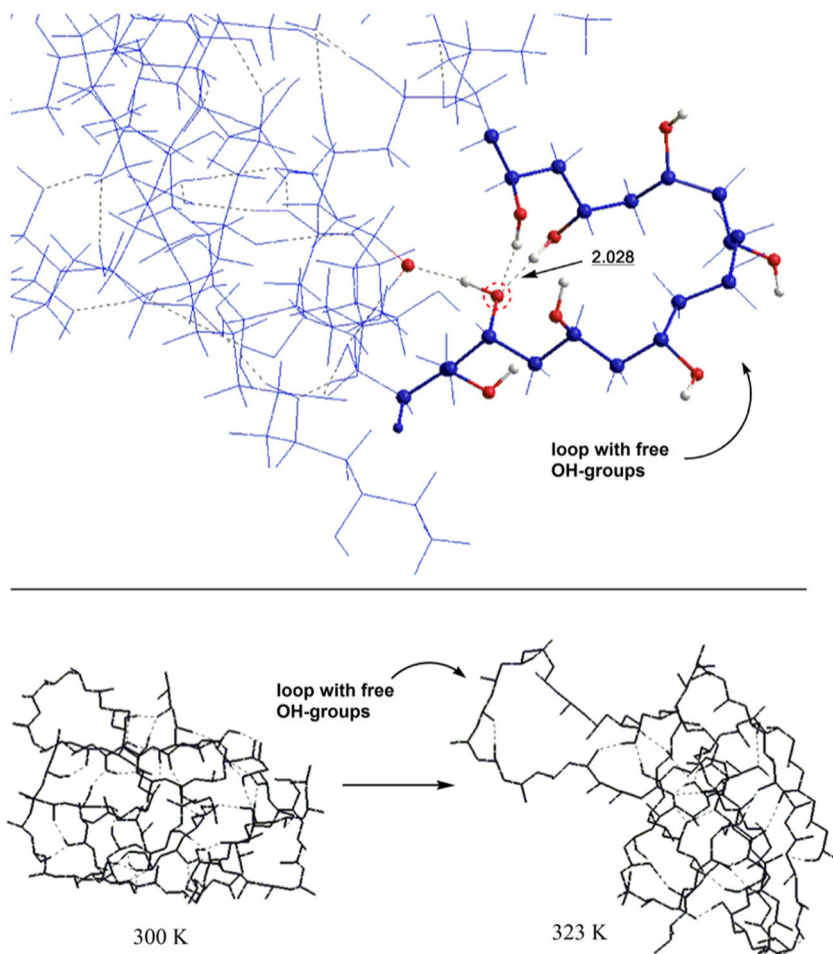
large number hydrogen bonds that stabilize the adopted conformation. Therefore, segments are forced to interact again with subsequent recombination of hydrogen bonds sometimes in the form of specific single-center domains demonstrated in Fig. 5. This effect is unique for polymeric systems especially for one with strong self-association ability as characterized by a delay in responding of the polymer system on change in temperature. This may also affect the slow response on some physical properties of the system until the critical temperature is reached. The average number of such bonds and, consequently, ΣD_{HB} does not change until a certain temperature is reached (T*). However, the average strength of hydrogen bonds constituting the domain decreases. Figure 5 also shows that length of hydrogen bonds typical for the loops is higher (2.028 Å) than the maximum average value of the hydrogen bond length $\langle d \rangle = 1.863$ Å (Fig. 3) calculated for the same polymer chain. Decrease in strength and density of hydrogen bonds within the coils while reaching the critical temperature (T*) increases the mobility of individual chain segments within the coils, which ultimately leads to an increase in the size of the coils (Fig. 6).

The formation of a looser conformation of the interacted coils is accompanied by the release of the chain fragments containing multiple "free" OH-groups turned off from the intra-chain interactions. Loops, shown in Fig. 5 further act as active centers of intermolecular association, which cause
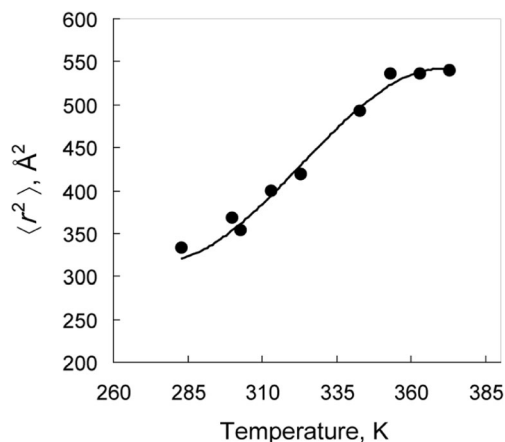

Fig. 6 The RMS distance between the ends of PVA chains $\langle r^2 \rangle$ as a function of temperature determined at the initial stage of interaction for the systems consisting of two coils

a sharp increase in D_{HB} values. Thus, using the data on the structural and dynamic characteristics of interacted PVA macromolecules one can conclude that changes in the structural organization of PVA-based solutions upon reaching the critical temperatures are associated with changes in the characteristics of hydrogen bonding in the polymeric system.

Summarizing the obtained data, two key stages responsible for the appearance of the described effect should be assigned. At the first stage, as the temperature increases, the length and, consequently, the strength of the intersegmental hydrogen bonds in the system decreases (Fig. 4). The total density of hydrogen bonds in the systems decreases when the critical temperature is reached, which is equal to ~330 K according to calculations. This is due to the weakening of hydrogen bonds formed between the segments of any individual coil. The decrease in strength and density of hydrogen bonds within PVA coils increases the mobility of individual units and entire segments within each of the coils. This ultimately contributes to an increase in the size of the coils with subsequent adoption of a loosely unwrapped (less dense) conformation. The formation of a looser conformation marks the beginning of the second stage, associated with a change in the conditions of interaction between two PVA chains. As shown above, the unfolding of the coil is accompanied by the release of loops ("free" fragments) turned off from the intracoil interactions possessing multiple unbonded OH-groups. Calculations revealed that under the specified conditions, the efficient way of lowering the energy for such formations is the interaction with functional groups of another macromolecule. This circumstance, in turn, can lead to an even greater stretching of the coils accompanied by a simultaneous increase in the contact area between them. For this reason, one can observe a sharp increase in the density of hydrogen bonds between the interacting coils, as well as a more rapid increase in the values of $\langle r^2 \rangle$ after reaching T*. An increase in the contact area and D_{HB} leads to a greater stabilization of the system, also making it more structured, which in turn favors the formation of intermolecular cross-links (Scheme 1).

## Effect of synthesis conditions on properties of the obtained PVB samples

If a cross-linking or potential cross-linking agent is added to a polymer solution, two different modes of cross-linking can be expected [2]. The first one is the cross-linking between different polymer molecules, termed inter-molecular cross-linking, which was described above. The second mode is the internal cross-linking of a single polymer chain, termed intramolecular cross-linking, which occurs when two nonconsecutive functional groups of one chain react in a cross-linking manner. It was previously reported [3, 6] that such bonds can form in polymer solutions, especially in dilute ones.

To study the effect of synthesis parameters on the properties of the obtained products, PVB samples were synthesized by varying the polymer concentration in various solvents at a temperature equal to 40 °C. The selected temperature represents the critical temperature corresponds to the maximum value of the reduced viscosity, recorded earlier during rheological experiments [4]. It was concluded that aqueous solutions of poly(vinyl alcohol) with 10 wt% of a co-solvent such as N-methylpyrrolidone and 1,4-butanediol are thermodynamically more favorable compared with binary poly(vinyl alcohol)/water systems. Hence, this provides the specific organization of the PVA-based solutions which theoretically should significantly reduce the possibility of intermolecular cross-linking. The characteristics of the synthesized copolymers (PVB with a low degree of acetalization) were studied using ^{1}H NMR, GPC, and by measuring the viscosity of diluted (1 wt%) polymer solutions in DMSO.

Figure 7 shows GPC curves obtained for initial (not modified) PVA and for PVB synthesized from a 5 wt% aqueous solution without addition of a co-solvent. Table 1 summarizes the data on characteristics of PVB samples synthesized under specified conditions. It can be seen that unmodified PVA is characterized by unimodal molecular weight distribution. Thus, the value of Mn was determined to be 11.7 kDa. However, for PVB with a degree of acetalization equal to 6.1% synthesized from semi-dilute 5 wt% aqueous solution (no co-solvent) the GPC curves show a well-defined bimodal character of the molecular weight distribution. In this case, the Mn of the first fraction (first mode) was determined to be 64.8 kDa. The average value of Mn for the first and second modes was equal to 13.3 kDa, and the polydispersity index Mw/Mn (Đ) was equal to 5.0, which also exceeded the values of Đ determined for pure PVA (Đ = 3.4). These data indicate that during PVB preparation in pure water, the increase in the molecular weights and Mw/Mn ratio of the resulting polymer occur. This should be addressed to the intermolecular cross-linking of the polymer chains.

To verify the effect of co-solvent schematically demonstrated in Scheme 1 we performed a series of experiments using aqueous solutions with 10 wt.% of 1,4-butanediol as co-solvent for the preparation of PVB samples. The results thus obtained indicate that isolated polymers are indeed characterized by narrower molecular weight distributions and lower molecular weights (Table 1).

As an alternative to the traditionally used low molecular weight catalysts (HCl, PTSA), a recently developed polymeric catalyst poly(N-(tert-octyl)acrylamide-co-2-acrylamido-5-(trifluoromethyl)pyridine) (Copolymer **1**) with a pronounced phase transition (UCST) in alcohol solutions was used [8]. This new approach based on the use of thermosensitive polymeric catalysts allows one to solve a complex problem of carrying out chemical reactions with high rate under homogeneous regime from the one side and to

high possibility of intermolecular cross-linking

low possibility of intermolecular cross-linking
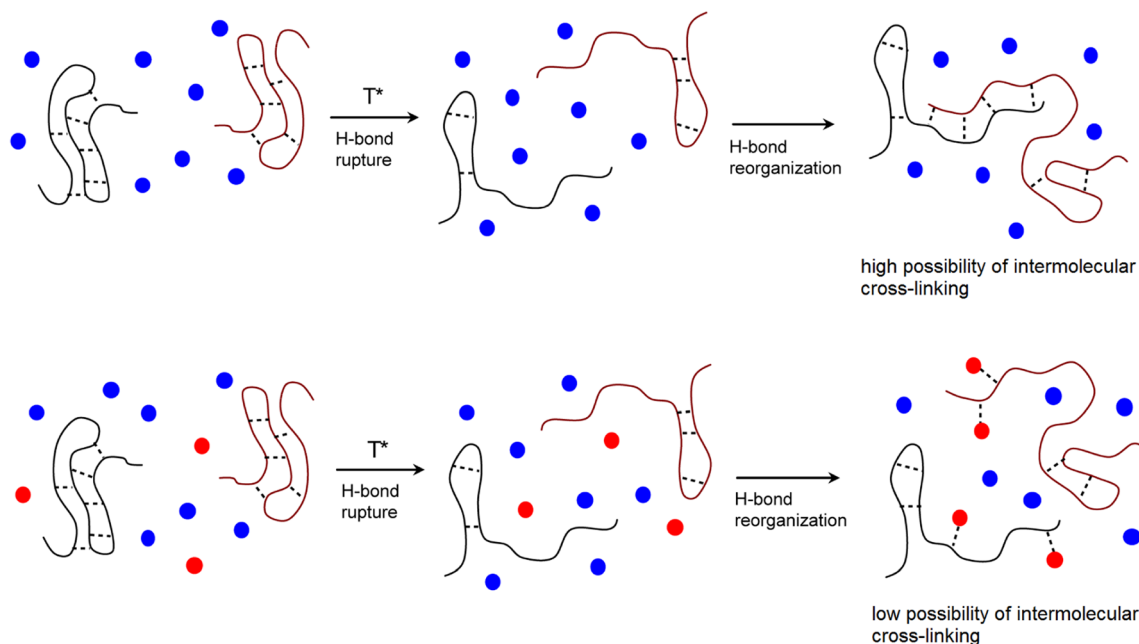
Scheme 1 Schematic representation of the proposed mechanism for the reorganization of hydrogen bonds in aqueous solutions of PVA upon heating (A) and alternative mechanism demonstrated previously [4] for the PVA-based solutions with thermodynamically favorable co-solvent. Blue balls – water molecules, red balls – co-solvent molecules. Associative interactions are shown by dashed lines.

realize a simple and efficient method of removal of the catalyst from the system after the completion of the process via the phase transition (precipitation) of the catalyst upon cooling. This will provide the solution to one of the general problems in using homogeneous catalysts – the complexity of their isolation and reuse. Additional experiments have shown that this polymeric catalyst is also soluble in DMSO, as well as mixtures of DMSO-THF and, as in the case with alcohols it demonstrates sharp phase transitions (UCST) in the indicated

DMSO-based solvents. Thus, in DMSO-THF (1/3 v/v) mixture, the UCST was determined to be around 70 °C (Fig. 8). It is remarkable that polymer readily precipitates from the DMSO-based solutions when cooled below the phase-transition temperature even from dilute solutions. A series of experiments using the proposed polymeric catalyst showed that PVB samples obtained under such conditions are characterized by a narrow polydispersity index equivalent to the one obtained for unmodified PVA. This circumstance indicates

Fig. 7 GPC traces obtained for unmodified (initial) PVA (solid line, Mw = 52 kDa, Mn = 11.7 kDa, Đ = 3.4) and PVB (dashed line, 1-mode: Mw = 70 kDa, Mn = 64.8 kDa; average (1 + 2 modes): Mw = 67 kDa, Mn = 13.3 kDa, Đ = 5.0), synthesized from binary 5 wt% PVA/ water solution
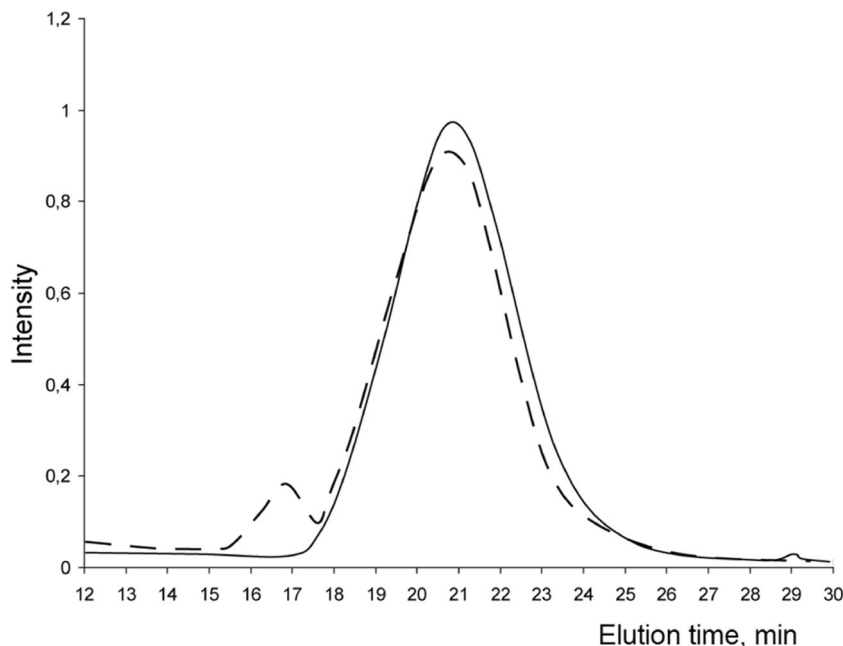
Table 1 Synthesis conditions and characteristics of the isolated PVB samples determined using ^{1}H NMR, GPC and viscometry measurements

PVA wt.%	Solvent	Catalyst	Degree of acetalyzation, %	Mw × 10^{-3}	Mn × 10^{-3}	Mw/ Mn	Viscosity, dl/g
10	DMSO-THF	Copolymer **1***	9.8	38.0	11.0	3.5	1.6
5	Water-1,4bdl**	HCl	7.7	42.0	10.5	4.2	1.42
5	DMSO	HCl	5.1	47.0	10.5	4.5	1.45
10	Water	HCl	2.5	52.0	12.4	4.2	2
5	Water	HCl	6.1	70.0	64.8	5.0	2.2
				67.0	13.3		

* Synthesis was carried out at 75 °C; * - 1,4-butanediol

that usage of this type of catalyst suppresses intermolecular acetalization reaction, which is likely due to the large volume of polymer catalysts creating steric hinders towards the interaction of two PVA chains and their subsequent cross-linking.

To confirm the described trends, a series of viscometric experiments were conducted to study the properties of the obtained PVB samples in dilute DMSO solutions. The literature data, as well as viscometric experiments carried out in the course of this work, allowed us to consider 1 wt% solutions to satisfy the requirement of isolation of macromolecular chains. The data obtained indicate that the highest viscosity was determined for the solutions of polymers synthesized in pure water. It can also be noted that for PVB samples synthesized in pure water, the viscosity values weakly depend on both the initial polymer concentration and the degree of acetalization (in the range 2.5–6%) and typically were found to be in the range of 2.0–2.2 dl/g. Compared to this system, solutions prepared from PVB samples synthesized from the mixed solvent and also in the presence of a polymeric catalyst **1** were found to be less viscous.

Thus, the analysis of the results of GPC and viscometry experiments showed that PVB samples synthesized in water in the absence of co-solvent additive are characterized by large molecular weights. Meanwhile, 1 wt% solutions of these polymers in DMSO were found to be the most viscous, which indicates a high probability of undesirable intermolecular acetalization taking place during the reaction. For such systems, the bimodal character of the molecular weight distribution was also observed on the GPC curves (Fig. 7), which indicates an increased heterogeneity of the final products. On the other hand, polymers synthesized from solutions with improved thermodynamics such as mixed solvents and also in presence of a new thermosensitive polymeric catalyst **1**, possess lower molecular weights and narrower molecular weight distribution. This indicates a sufficient decrease in the degree of intermolecular cross-linking of PVB chains under given conditions.

Conclusions

It was demonstrated using LD that differences in strength of hydrogen bonds realized in PVA-based systems are responsible for the conformation of a dense coil adopted by the macromolecule in dilute regime. Stabilized by numerous hydrogen bonds, the compressed conformation is energetically more favorable under conditions when water is used as a solvent. However, reaching a critical concentration, macromolecular coils begin to overlap with subsequent reorganization of part of the intramolecular hydrogen bonds formed within a single coil into intermolecular hydrogen bonds.

The analysis of the dynamics of the structural factors was carried out as a function of temperature to establish the mechanism of structural reorganization for the PVA-based systems under conditions of interacted coils. Interestingly, it was demonstrated that no uniform decrease in the total density of hydrogen bonds is observed, as one could expect based on the sensitivity of hydrogen bonds with respect to temperature. This "delay" effect was attributed to specific properties of polymeric systems with strong intersegmental association and characterized by a delay in responding of the polymer system on change in temperature. It was also shown that the decrease in strength and density of hydrogen bonds within
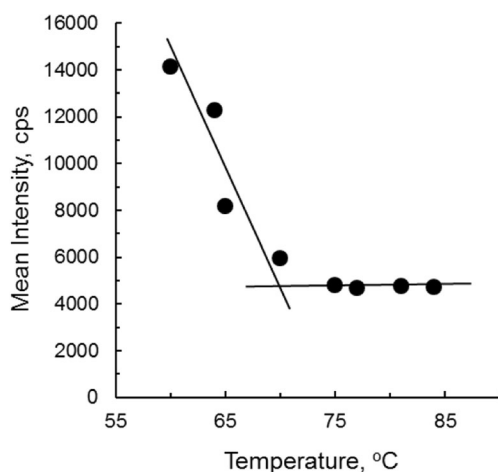

Fig. 8 Mean intensity determined by DLS as a function of temperature for 0.1 wt% solution of catalyst **1** in DMSO-THF (3/1 v/v) mixture demonstrating phase separation (UCST) at around 70 °C

PVA coils while reaching the critical temperature (T*) increases the mobility of individual chain segments within the coils, which ultimately leads to an increase in the size of the coils. The unfolding of the coil is accompanied by the release of loops ("free" fragments) turned off from the intracoil interactions possessing multiple unbonded OH-groups. This circumstance, in turn, can lead to an even greater stretching of the coils accompanied by a simultaneous increase in the contact area between them. It was assumed that an increase in the contact area between PVA coils favors the formation of intermolecular cross-links. The assumptions made in this and also in previous papers were finally proved experimentally. It was demonstrated that synthesis carried out in pure water lead to the formation of less homogeneous PVB samples. In contrast to this target polymers prepared from ternary water/co-solvent/PVA solutions and also in presence of new thermosensitive polymeric catalyst were found to possess lower molecular weights and narrower molecular weight distribution.

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