

Viscometric and light scattering investigation of the hydrogen bonds in the solutions of polycarbinol

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Received: 8 December 2011 / Accepted: 29 May 2012 / Published online: 24 June 2012
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Abstract The nature of hydrogen bonding in methanol solutions of Polycarbinol was investigated by the methods of Viscometry and Light scattering. The intrinsic viscosity (η) of narrow fraction of Polycarbinol in methanol in presence of various amounts of hydrogen bond acceptor—sodium hydroxide (NaOH) was determined using Viscometry. It was established that the values of with addition of are passing through the extreme values due to the fact that intermolecular hydrogen bonds are broken first resulting in the decrease of, and then break in intramolecular hydrogen bonds is leading to increase of. Huggins constant reaches maximum value at complete suppression of intermolecular hydrogen bonds. Results of Light scattering show that the addition of an acceptor hydrogen bonds decreases the mean-square radii of gyration symbatically to values. The most compact size of macromolecules corresponds to minimum of values.

Keywords Hydrogen bonds · Viscometry · Light scattering · Coatings

Introduction

Many polymers are strengthened by hydrogen bonds (HB) in their main chains. Different methods of research of polymers in solutions can be used to study intra- and intermolecular associations of macromolecules. The investigation of the associative phenomena in solutions of polymers became a subject of numerous researches [1–13], including theoretical [1–6]. The intra- and intermolecular HB have been investigated by the method of IR spectroscopy [7–9]. Methods that are especially successfully applied to study HB in solutions of polymers are Viscometry and Light scattering [10–13]. We will also notice, that the methods noted above allow to successfully define the characteristics of HB in macromolecules.

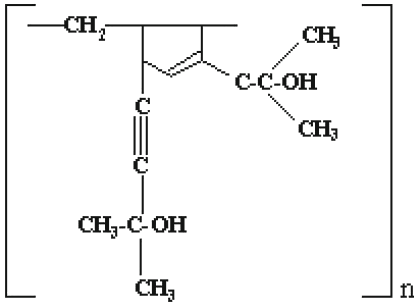
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The aim of the present work was to investigate the nature of HB in methanol solutions of PC by Viscometry and Light scattering.

Experimental section

Policarbinol (Polydimethylvinylethynylcarbinol) was synthesized by radical polymerization of Dimethylvinylethynylcarbinol $[\text{CH}_2 = \text{CH} - \text{C} \equiv \text{C} - (\text{CH}_3)_2\text{OH}]$ using



benzoic peroxide as an initiator. This polymer is recommended for use as a varnish for high-quality parquet. The synthesis of the Polycarbinol (PC) has been described in detail in a previous publication [15]. Below is a formula of PC.

As it is known, the associative phenomena in solutions of polymers are basically observed in the presence of specific functional groups as a part of the macromolecules capable of HB formation. In our case those are two hydroxyl groups of the monomer unit of PC.

We have studied characteristics of HB in macromolecules of PC by the combination of Viscometry and Light scattering methods.

Intrinsic viscosity measurements were performed in methanol at 20 °C using an Ubbelohde type capillary viscometer (the capillary's diameter 0,56 mm). The viscometers used were calibrated over the required temperature range. Measurements were made in a thermostat, the temperature of which could be maintained within the range of ± 0.01 °C of the required value. The dimensions of capillary of the viscometers used were selected to avoid shear effect. The efflux time of solvent was 108 s. Efflux times were obtained with an accuracy of ± 0.04 %. The solvent and solutions were filtered through a No.3 glass filter before the measurements. We investigated the dependence of reduced viscosity on concentration. The intrinsic viscosities ($[\eta]$) of PCs were estimated by the extrapolation of reduced viscosity to zero concentration.

The data were analyzed according to Huggins equation [14]:

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C,$$

where η_{sp}/C is the specific viscosity, $[\eta]$ is the intrinsic viscosity, K' is the Huggins constant and C concentration of solution.

Light scattering measurements were performed in methanol at 20 °C on the Light scattering instrument FPS -3 (constructed by the Central Constructional Bureau of

Academy of Sciences, USSR) with unpolarized incident light ($\lambda=436$ nm). Scattering intensities were measured over the angular range $30\text{--}150^\circ$ with benzene as a reference ($I_u=48,5 \times 10^{-6} \text{ cm}^{-1}$).

The refractive index increment ($\partial n/\partial c$) was measured on a Pulfrich differential refractometer in methanol at 20°C by using mercury-discharge lamp with blue light (435, 8 nm), giving $\partial n/\partial c=0,175 \text{ cm}^3 \text{ g}^{-1}$. For purification purposes the solvent and solutions were filtered directly in the measuring cells through the glass filters of different sizes (No. 4–5) at room temperature.

The mass-average molecular mass (\overline{M}_w), mean-square radii of gyration (\overline{R}^2)^{1/2} and second virial coefficient (A_2) of PC in a given solvent were evaluated using well-known expressions of classical Light scattering [14]:

$$\frac{KC}{R(\theta)} = \frac{1}{MP(\theta)} + 2A_2C,$$

where $K = \frac{4\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2}{\lambda_0^4 N_A}$ is the optical constant, with C , n_0 , λ_0 and N_A the polymer concentration, solvent refractive index, the wavelength of the incident beam, and Avogadro's number, respectively.

The (\overline{M}_w), (\overline{R}^2)^{1/2} and A_2 of PC in methanol were determined by Zimm method [14].

Values of R were calculated from inclinations S_0 of curves $\left(\frac{KC}{R(\theta)}\right)_{c \rightarrow 0}$ and A_0 segments, cut by these curves on axes of ordinates, on dependence [14]:

$$\frac{S_0}{A_0} = \frac{1}{3} R^2 \frac{16\pi^2}{\lambda^2},$$

where λ is the wavelength of diffused light.

Viscometry and Light scattering were performed by the method of the isoionic dilution of Pals and Herman's [16].

The experimental errors were in allowed limits of appropriate methods and did not exceed 1 % for Viscometry and 9 % for Light scattering measurements.

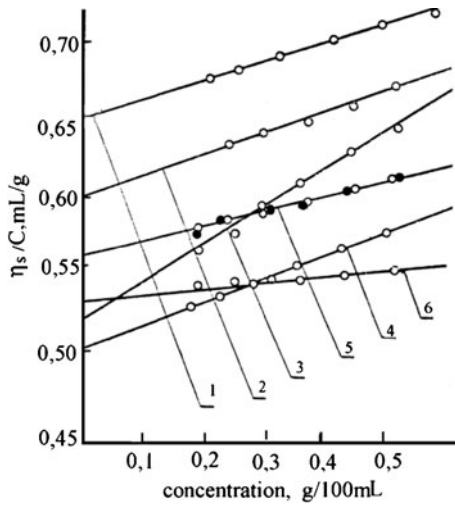
Results and discussion

Results of definition of $[\eta]$ for narrow fraction of PC in a pure methanol and at addition in methanol solutions of a well-known acceptor of HB - $NaOH$ are given on Fig. 1.

The values of experimentally derived $[\eta]$ and calculated K' for PC in pure methanol solution and upon addition of various amounts of $NaOH$ are given in the Table 1.

Using Light scattering method in the same conditions \overline{M}_w , (\overline{R}^2)^{1/2} and A_2 of the same fraction PC were defined at corresponding extreme values of $[\eta]$ in methanol and upon addition of certain quantities of $NaOH$. Results of these definitions are given on Fig. 2.

Fig. 1 Dependence $\frac{\eta_{sp}}{C} = f(C)$ for PC in methanol at molar ratio of *NaOH/PC*: 1 - 0; 2 - 0,17; 3 - 0,25; 4 - 0,5; 5 - 1,0 and 1,5; 6 - 2,5



The derived \overline{M}_w , $(\overline{R}^2)^{1/2}$ and A_2 values, together with the viscosity data are summarized in Table 1.

Figure 3 shows the variation of $[\eta]$ as well as K' with the degree of eliminated HB. As it is seen from Fig. 3 upon addition of *NaOH* the value $[\eta]$ passes through extreme values. Apparently, at first intermolecular HB brake off due to decrease of $[\eta]$, and then intramolecular HB break due to increase of $[\eta]$. Chains with only intramolecular HB would be more compact. This would result in lower $[\eta]$ and $(\overline{R}^2)^{1/2}$ as it is seen from Fig. 3.

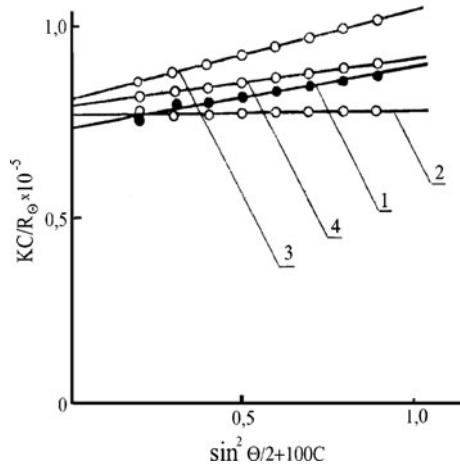
At the further addition of *NaOH*, $[\eta]$ slightly decreases—apparently due to deterioration of solvent quality, and then stays relatively constant, due to full suppression of HB. We have defined thermodynamic properties of the solvent from the comparison of A_2 values of PC samples derived in different solvent composition.

The behavior of Huggins constant is remarkable. As seen from Fig. 3, K' reaches the maximum value at full suppression of intermolecular HB. This result can be

Table 1 Values of experimental $[\eta]$, \overline{M}_w and calculated values K' , $(\overline{R}^2)^{1/2}$ and A_2 of PC in methanol and at presence of various amounts of *NaOH*

$\frac{NaOH}{PK}, \frac{mol}{mol}$	$[\eta], dl/g$	K'	$\overline{M}_w \times 10^{-5}$	$(\overline{R}^2)^{1/2}, \text{\AA}$	$A_2, \frac{mol \cdot ml}{g^2}$
0,00	0,650	0,307	1,33	38,8	1,41
0,17	0,600	0,416	—	—	—
0,25	0,520	0,945	—	—	—
0,50	0,500	0,740	1,28	20,1	1,51
1,00	0,560	0,314	—	—	—
1,25	0,570	0,281	1,22	34,2	1,35
1,50	0,560	0,250	—	—	—
2,50	0,515	0,205	1,25	31,7	1,27
3,50	0,515	0,205	—	—	—

Fig. 2 Dependence $\frac{KC}{R_{\theta}} = f \times (\sin^2 \frac{\theta}{2} + 100C)$ for PC in methanol at molar ratio of NaOH/PC: 1 - 0; 2 - 0,5; 3 - 1,25; 4 - 2,5



correlated with physical sense of this characteristic, according to which at identical values of molecular weight the highest values of K' are reached at the most compact conformation of macromolecules.

As it is seen from the data of Table 1 \overline{M}_w practically does not change, the change in $(\overline{R}^2)^{1/2}$ and A_2 are consistent with the change in viscosity.

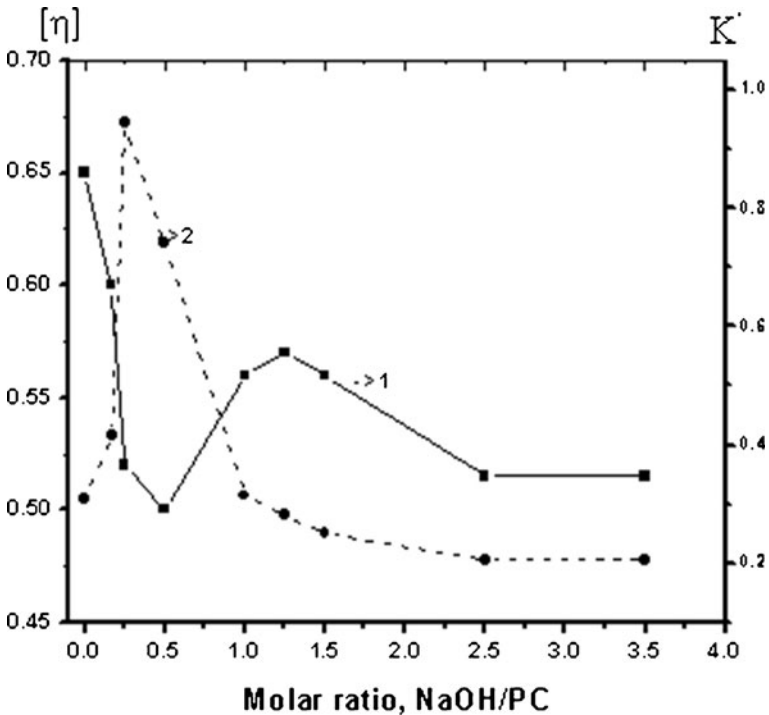


Fig. 3 Dependence of (1) $[\eta]$ and (2) K' on the molar ratio NaOH/PC

Thus, it can be concluded, that the addition of HB acceptor lowers the values of $(\overline{R^2})^{1/2}$ symbatically to $[\eta]$ values.

The minimum value of $(\overline{R^2})^{1/2}$ is reached at full suppression of intermolecular HB.

Conclusion

The results of Viscometry and Light scattering investigations of nature of hydrogen bonding(HB) in methanol solutions of Policarbinol(PC) are described in this paper. It was established that both intra- and intermolecular hydrogen bonding exist in macromolecules of PC. Depending on degree of elimination of HB by application of HB acceptor (*NaOH*), conformational transmission in PC macromolecules is observed. With addition of *NaOH* the intermolecular HB are broken first which leads to diminished size of macromolecules. Further addition of *NaOH* leads to breaking of intramolecular HB leading to increase of macromolecules. Huggins constant reaches maximum value at complete suppression of intermolecular HB. Results of Light scattering show, that the addition of an acceptor HB lowers the mean-square radii of gyration symbatically to $[\eta]$ values. The most compact size of macromolecules corresponds to the minimum of $[\eta]$ values.

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