



UNIVERSITY OF NIŠ

The scientific journal FACTA UNIVERSITATIS

Series: Working and Living Environmental Protection Vol. 1, No 3, 1998, pp. 25 - 32

Editor of series: Ljiljana Rašković, e-mail: ral@kalca.junis.ni.ac.yu

Address: Univerzitetski trg 2, 18000 Niš, YU, Tel. +381 18 547-095, Fax: +381 18 547-950

http:// ni.ac.yu/Facta

INVESTIGATION OF CONFORMATIONAL CHARACTERISTICS OF UNTOXIC WATER-SOLUBLE COPOLYMERS FOR APPLICATIONS IN DYES AND LACQUERS INDUSTRY

UDC:667.62

Suzana Cakić, Ljiljana Rašković, Dragan Đorđević

Faculty of Technology, Leskovac, Bulevar oslobodjenja 124, 16000 Leskovac

Abstract. *In this paper the conformational characteristics of two sample (PAA-A-120 and PAA-A-150) of copolymers [poly(acrylamide-co-acrylic acid)] were studied by using rectangular pulses. The results of this investigations shows that these copolymers have the conformational characteristics (great chains flexibility) enabling their applications in dye and lacquers industry like water-soluble systems. The investigated copolymers might be an emulgations or dispersions in the recaptures for dyes and lacquers, since they are water-soluble, the organic solvents are not present.*

1. INTRODUCTION

Electric birefringence (EB, the Kerr effect) is an important method for investigation of conformational, electro-optical and electrodynamic properties of polymers in solutions. The method is particularly successful for polymers soluble in non-polar solvents. The deformation of electro-optical signal which depends on the time of duration of rectangular electric pulse, concentration and temperature of the solutions, is probably due to change in the conformation of the molecules [1-5].

When the rectangular-pulse procedure is used for kinetically rigid axially symmetrical polar molecules, the variation in EB $\Delta n(t)$ during the time t is determined by the equation [6,7]:

$$\frac{\Delta n(t)}{\Delta n_0} = \int_0^{\infty} \varphi(\tau) f(t, \tau) d\tau \quad (1)$$

where the function $\varphi(\tau)$ takes into account the contribution to EB of molecules with relaxation time in the range from τ to $\tau + d\tau$:

$$\begin{aligned}
 f(t, \tau) &= \exp(-3t/\tau) \text{ for the decay;} \\
 f(t, \tau) &= 1 - 1.5 \exp(-t/\tau) + 0.5 \exp(-3t/\tau) \text{ for the rise}
 \end{aligned}
 \tag{2}$$

τ is the relaxation time proportional to the frictional coefficient W of molecule in its rotation around the axis normal to molecular dipole: $\tau = W/2kT$

k – Boltzmann constant, $1.38 \cdot 10^{-23} \text{JK}^{-1}$;

T – temperature, (K);

The areas Q_R and Q_D limited by this theoretical curve for a monodisperse substance according to equation (1) are given by

$$Q_R = \int_0^{\infty} [1 - \Delta n(t)/\Delta n_0] dt; \quad Q_D = \int_0^{\infty} \Delta n(t)/\Delta n_0 dt
 \tag{3}$$

According to equation (1) – (3) for a monodisperse polymer, we have for the decay curve

$$Q_D = \tau / 3 = W / 6kT = \tau_0 \quad (\tau_0 - \text{time of "free relaxation"})
 \tag{4}$$

and for tend for the rise curve

$$Q_R = 4\tau / 3 = 2W / 3kT = 4Q_D
 \tag{5}$$

When polydispersity of molecular weighs M exists, there is a change of Q_R and Q_D (in this case $Q_D = \langle \tau_0 \rangle$ is the mean time of free relaxation).

However, according to equations (1) – (3), their ratio remains invariable: $Q_R/\langle \tau_0 \rangle = 4$ regardless of the type function $\varphi(\tau)$.

For kinetically rigid chain, the relaxation time is known to be related to M , $[\eta]$ and the solvent viscosity η_0 by the equation

$$\tau = W / 2kT = M[\eta]\eta_0 / 2FR T
 \tag{6}$$

R – $8.314 \text{JK}^{-1}\text{mol}^{-1}$;

Here, the coefficient F depends on hydrodynamic properties of particle representing the molecule and has limiting values $F = 2/15 = 0,133$ for a thin rod and $5/12 \approx 0,42$ for spherical globule.

2. EXPERIMENTAL

The measurements of EB were carried out with two samples of copolymers: poly(acrylamide-co-acrylic acid) with commercial nomenclature: PAA-A-120 and PAA-A-150.

These copolymer solutions in redistilled water were investigated at room temperature and interval from 18°C to 50°C .



The method and apparatus for measurements have been well described [8]. The Kerr cell was made from metal electrodes 7,46 cm in length along the beam path and a gap between them of 0,14 cm. The voltage fed to the electrodes did not exceed 1500 V. The experimental results have been obtained by the Brice's method [8].

The molecular weights M_V of these copolymers were determined from intrinsic viscosity $[\eta]$ (extrapolated to zero rate gradients) in water with aid of the equation [9]:

$$[\eta] = 6,31 \cdot 10^{-3} M^{0,8} \text{ cm}^3/\text{g} \quad (7)$$

3. RESULTS AND DISCUSSION

The obtained results show that electric birefringence is negative in solutions of two investigated samples of copolymers and is not proportional to E^2 (electric field strength) in the range of the low applied electric field strength ($E^2 = 2 \cdot 10^8 \text{ [Vm}^{-1}]^2$, Fig. 1a). Electric birefringence is positive in solutions of two samples at the range of higher applied electric field strength. ($E^2 = 2 \cdot 10^{10} \text{ [Vm}^{-1}]^2$, Fig. 1b). The elektro-optical signal under the same experimental conditions is same for second investigated sample (PAA-A-150).



Fig. 1. Electro-optical signal in the solution with $c = 0,1 \cdot 10^{-4} \text{ gcm}^{-3}$ of PAA-A-120 at time duration of rectangular electric pulse $t_w = 1 \text{ ms}$, temperature $T = 25,4^\circ\text{C}$ and the electric field strength: a) $E^2 = 2 \cdot 10^8 \text{ [Vm}^{-1}]^2$; b) $E^2 = 2 \cdot 10^{10} \text{ [Vm}^{-1}]^2$

Electro-optical signal starts to deform for solutions of two copolymers at the range of high applied electric field strength with the rise of the time duration of rectangular electric pulse (Fig. 2.)

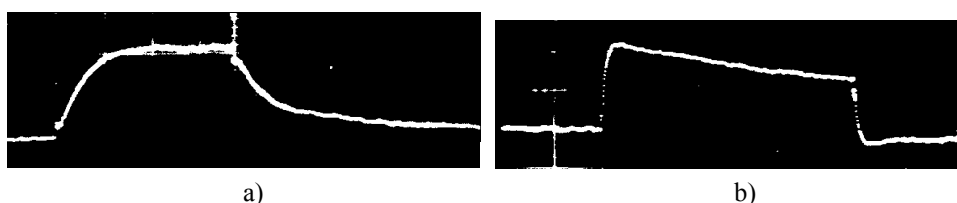


Fig.2. Electro-optical signal in the solution with $c = 0,05 \cdot 10^{-4} \text{ gcm}^{-3}$ of PAA-A-120 at the electric field strength: $E^2 = 11,5 \cdot 10^{11} \text{ [Vm}^{-1}]^2$, times of duration of rectangular electric pulse are: a) $t_w = 500 \text{ } \mu\text{s}$; and b) $t_w = 2 \text{ ms}$; at temperature $T = 25,4^\circ\text{C}$.

The higher field strengths increase the electric birefringence. The critical supermolecular structure formation is $0,34 \cdot 10^{-4} \text{ g/mol}$ (Fig. 3).

Two factors cause increase of Δn EB with temperature: the higher kinetic energy of the particles and the higher dissociation, causing increased number of the particles in the solution.

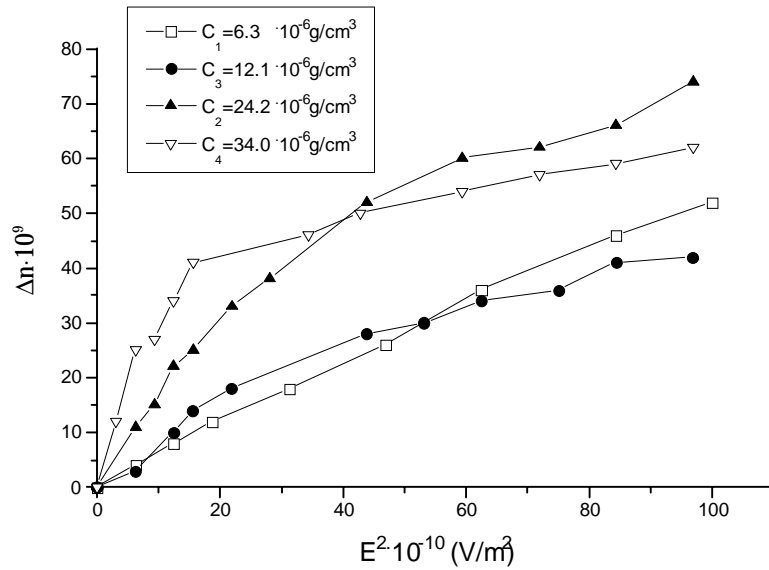


Fig. 3. Δn EB of solutions of PAA-A-120 vs square of electric field strength (E^2) at various concentrations of solutions and constant temperature ($T = 24.6 \text{ }^\circ\text{C}$)

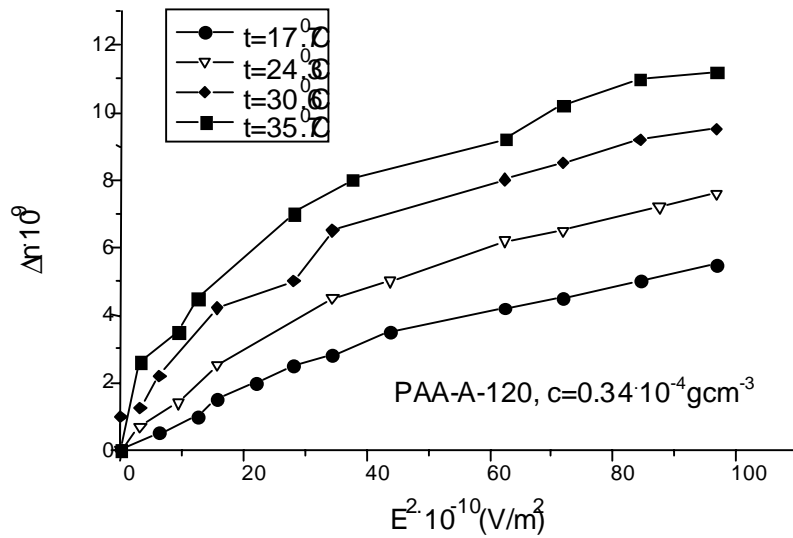


Fig. 4. Δn EB of solution with concentration $c = 0.34 \cdot 10^{-4} \text{ gcm}^{-3}$ of PAA-A-120 vs square of the electric field strength (E^2) at various temperatures

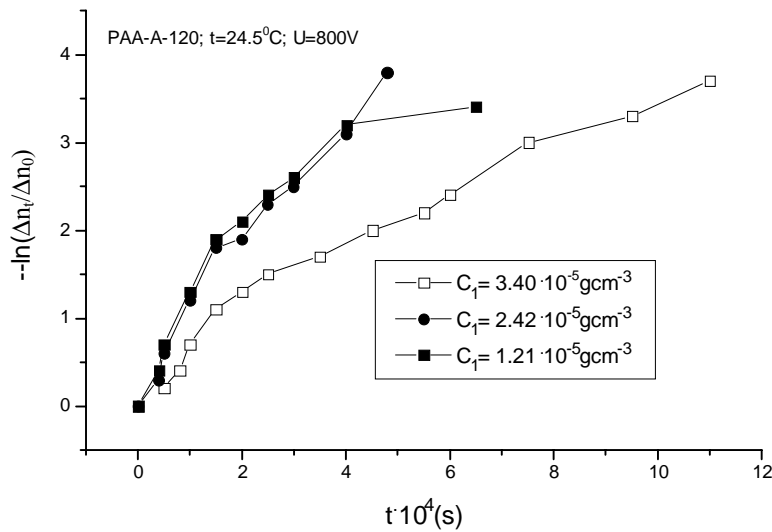


Fig. 5. The birefringence decay curves of samples of solutions of PAA-A-120 at $E^2 = 32.6 \cdot 10^{10} [\text{V/m}]^2$ and temperature $T = 24.5^{\circ}\text{C}$

The logarithm, Δn_t , relative to the steady state birefringence Δn_0 , is plotted vs time after removing of electric field.

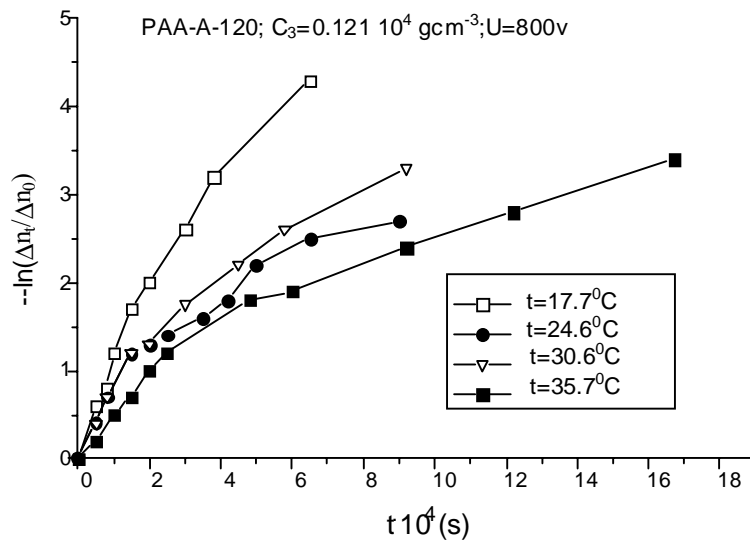


Fig. 6. The birefringence decay curves of EB (Δn) of solution with concentration $c = 0.121 \cdot 10^{-4} \text{gcm}^{-3}$ of PAA-A-120 vs square of the electric field strength ($E^2 = 32 \cdot 10^{10} [\text{V/m}]^2$) at various temperatures.

The comparison of the curves on fig. 5 and fig. 6 suggests that at the field strengths higher ($E^2 = 32 \cdot 10^{10} [\text{V/m}]^2$), the equilibrium in the system is established faster, that is, the relaxation time are shorter due to the higher orientation effect causing decrease of the interactions of the macromolecules.

Table 1. Electro- optical characteristics of the solutions, of PAA-A-120 at $t_w = 500\mu\text{s}$; $T = 24.3^\circ\text{C}$ and $E^2 = 11.5 \cdot 10^{11} [\text{V/m}]^2$

$C \cdot 10^4$ (gcm^{-3})	$Q_R \cdot 10^5$ (s)	$Q_D \cdot 10^5$ (s)	Q_R/Q_D	$\langle \tau_0 \rangle \cdot 10^6$ (s)	$\langle \tau_0 \rangle_{c \rightarrow 0} \cdot 10^6$ (s)	$Q_R / \langle \tau_0 \rangle_{c \rightarrow 0}$
0.121	4.12	7.66	0.537	96.8		
0.242	4.48	4.26	0.114	80.0	141	0.202
0.340	3.37	5.07	0.665	51.9		

An increase of the PAA-A-120 concentration decrease the relaxation time, probably due to the higher effect of orientation of the permanent and the induced dipoles in macromolecules, which lower relaxation time.

Table 2. Electro- optical characteristics of the solutions, $c = 0.121 \cdot 10^{-4} \text{gcm}^{-3}$ of PAA-A-120 at $t_w = 500\mu\text{s}$

T ($^\circ\text{C}$)	$E^2 = 11.5 \cdot 10^{11} [\text{V/m}]^2$				$E^2 = 32.6 \cdot 10^{10} [\text{V/m}]^2$			
	$Q_R \cdot 10^5$ (s)	$Q_D \cdot 10^5$ (s)	Q_R/Q_D	$\langle \tau_0 \rangle \cdot 10^6$ (s)	$Q_R \cdot 10^5$ (s)	$Q_D \cdot 10^5$ (s)	Q_R/Q_D	$\langle \tau_0 \rangle \cdot 10^6$ (s)
17.7	4.02	10.52	0.382	201.1	4.79	8.60	0.56	163.6
24.3	4.70	14.90	0.315	199.3	6.34	17.80	0.36	197.0
30.6	5.70	16.80	0.339	362.5	6.13	17.50	0.31	301.5

At the lower field strength (tab.2), increases the relaxation time with temperature increase due to the disorientation effect of chaotic (PAA-A-120). Heat moving and increased number of collisions. However, at higher field strength, the relaxation time variations are taking place, which is connected with two processes taking place: the orientation of ionic groups under the influence of the electric field, and the disorientation due to the heat moving.

Table 3. Electro- optical characteristics of the solutions, $c = 0.101 \cdot 10^{-4} \text{gcm}^{-3}$ of PAA-A-150 at $t_w = 500\mu\text{s}$

T ($^\circ\text{C}$)	$Q_R \cdot 10^5$ (s)	$Q_D \cdot 10^5$ (s)	Q_R/Q_D	$\langle \tau_0 \rangle \cdot 10^6$ (s)
17,9	5,10	11,00	0,463	248,5
24,5	4,98	9,48	0,506	227,8
28,4	5,47	12,10	0,452	286,4
34,3	6,06	12,00	0,502	281,0
39,4	5,41	39,40	0,137	276,0

The temperature changes (PAA-A-150, tab.3) do not cause higher variation of the relaxation time (probably due to the higher number of ionogenic groups).

Table 4. The values of F obtained according to the equations (7) at T = 25°C

Samples	M_v (g/mol)	$[\eta]$ (cm ³ /g)	$\langle\tau_0\rangle_{c \rightarrow 0} \cdot 10^6$ (s)	F
PAA-A-120	$8.2 \cdot 10^7$	$1.350 \cdot 10^4$	137	391
PAA-A-150	$8.3 \cdot 10^7$	$1.370 \cdot 10^4$	141	498

The obtained results show that the conformational characteristics of these copolymers indicates the possibility of their applications as water-soluble systems in dye and lacquers are responsible for achievement of necessary adhesivity to different materials (metal – wood). In other hand, the conformational characteristics defined the behavior of copolymers in a solution where other components are present. That is components make the formulation of dyes and lacquers. Those copolymers might be an emulgations or dispersions in the recaptures for dyes and lacquers. Since they are water-soluble the organic solvents are not present.

4. CONCLUSIONS

The values of electro-optical characteristics obtained for the investigation samples are different from those of kinetic rigid-chain polymers ($Q_R/Q_D \approx 4$; $Q_R/\langle\tau_0\rangle_{c \rightarrow 0} \approx 3$ [10]). They show that the processes of induced dipole orientation of macromolecules in the electric field occur at higher rate than those of their disorientation (free relaxation of EB) in absence of the field as compared to the situation observed for kinetically rigid chains. This result may be interpreted as a manifestation of the local motion (kinetic flexibility) of polymer chain under the influence of the electric field.

The addition of component which approved the shining those copolymers can be used as water-soluble lacquers. The results show that since the copolymers posses a great chains flexibility those used in dyes and lacquers industry.

REFERENCES

1. Tsvetkov N. V., *Rigid-Chain Polymers*, Plenum Press, New York, pp. 8-13, 1989.
2. O'Konski T.C., *Molekular Electro-Optics*, Vol. 1, 2 pp. 34- 39, 1978.
3. Shashona N.V., *J. Am. Chem. Soc.*, 81, pp.3156- 3163, 1959.
4. Hagerman J. P. and Zimm H.B., *Biopolymers*, 20, pp. 1481-1487. 1981.
5. Tsvetkov N. V., *Vysokomol. Soedin.*, A 29, pp. 995-999, 1987.
6. Benoit H V., *J. Chim. Phys.*, 47, pp. 719-725, 1950.
7. Fredericq E. and Houssier C., *Electric Dichroism and Electric Birefringence*, Oxford University Press, London, , pp. 123-129, 1973.
8. Andonovski A., Bahčevandžiev S. i Geršanovski D., *Bilten na SDF na SRM*, 23, pp. 34-35, 1984/85.
9. Brandrup J. and Immergut H. E., *Polymer Handbook*, John Wiley and Sons, New York, pp. 234-239, 1985.
10. Tsvetkov V N et al ., *Eur. Polym. J.*, 2, pp. 163-168, 1990.

**ISPITIVANJE KONFORMACIONIH KARAKTERISTIKA
NETOKSIČNIH VODORASTVORNIH KOPOLIMERA
ZA PRIMENU U INDUSTRIJI BOJA I LAKOVA**

Suzana Cakić, Ljiljana Rašković, Dragan Đorđević

U ovom radu ispitivane su konformacione karakteristike dva uzorka (PAA-A-120 i PAA-A-150) kopolimera (akrilamid-akrilna kiselina) korišćenjem pravougaonih električnih impulsa. Rezultati ovih ispitivanja pokazuju da ovi kopolimeri imaju veliku fleksibilnost lanaca koji omogućavaju njihovu primenu u industriji boja i lakova u vodorastvornih sistema. Ispitivani kopolimeri mogu biti emulgjuća tj. disperziona sredstva u recepturi boja i lakova, pa kako su vodorastvorna time je eliminisano učešće organskih rastvarača.