

## Viscous Behavior of Dilute CMC Salt Solution Before and After Photodegradation

F. EL-Ashhab, L. Sheha, R. M. Sheltami, and Z. M. Feituri

Chemistry Department, Faculty of Science, Garyounis University, Benghazi, Libya P. O. Box 5758, Benghazi, Libya

e-mail: academiapolymerica@yahoo.co.uk

### السلوك اللزج لمحلول الكربوكسي ميثيل سليولوز الملحي المخفف قبل و بعد تعرضه للانحلال الضوئي

فتحي الأشهب, لبنى عبد العزيز شيحا, رشا محمد الشلطامي و زكريا الفيتوري

قسم الكيمياء - كلية العلوم - جامعة قاريونس بنغازي- ليبيا

تم دراسة منحنى الانحلال الضوئي للكربوكسي ميثيل سليولوز (CMC) بمحلوله المائي . أجريت قياسات الكثافة و اللزوجة ل CMC ( المتواجد في محلول ملحي ) بمنطقة التركيز المخفف جداً قبل و بعد تعرضه للأشعة فوق البنفسجية. لوحظ أن هذه الأشعة تقلل من قيم الكثافة، اللزوجة النوعية، اللزوجة المختزلة و اللزوجة الجوهرية، و كذلك الكتلة المولارية و الحجم الهيدروديناميكي و معامل التمدد و أيضاً الأبعاد الحقيقية و المثالية لسلسلة ال CMC في المحلول. بينما زاد تفاعل المذاب مع المذيب و قل اتصال جزيئات المذاب مع بعضها الآخر في المحلول المنحل للكربوكسي ميثيل سليولوز بسبب تأثير أشعة UV .

Key words: *Density, Huggins-Kraemer Equations, Photodegradation, Solution Viscosity, Very Dilute Solution.*

#### ABSTRACT

Photodegradation curve of carboxymethylcellulose (CMC) in aqueous solution has been reported. Densities and solution viscosities of very dilute CMC salt solution before and after UV-irradiation have been measured. UV-irradiation of CMC decreases the values of density, specific, reduced and intrinsic viscosities, molar mass, hydrodynamic volume, expansion factor, real and ideal chain dimensions of CMC in solution. In contrary, it increases the solute-solvent interaction and decreases the solute-solute contact in the solution of degradable CMC.

#### Introduction

Most of natural and non-protected synthetic or semi synthetic polymers undergo photo- rheological change when exposed to ultraviolet (UV) radiation [1-5], a major cause of such change is the main chain scission or crosslinking and, as a result, the molecular dimensions of the polymer conformational state, also, change [2-5].

CMC is one of those non-protected semi synthetic polymers [6, 7]. Although, the effects of high-energy radiation on sodium carboxymethylcellulose were investigated, studies in photo-rheology of CMC have escaped the attention of the workers [5,7- 10]. In our present investigation, we report the effect of photolysis on real and ideal viscous behavior of CMC in very dilute salt solution.

## Experimental

### Material and mother solution

The powder material of CMC supplied by local Libyan company (JOWF) and used without further purification. Mother solution of  $1 \text{ kg m}^{-3}$  concentration was prepared by adding a known weight of the polymer to fixed volume of a double distilled water and dissolving with magnetic stirring, giving a clear solution. Some extra double distilled water was, then, added up to the required volume and the solution was divided to equal volumes.

### UV- irradiation

Mother solution samples were irradiated in air at room temperature by a Low Pressure Mercury Lamp, Type 93110, E27 of spectral lamp company,  $\lambda = 185 \text{ nm}$  and  $P = 6\text{W}$ . Each sample was exposed to the UV-irradiation at same condition for different period of time. Monitoring the change in each sample was immediately after irradiation, and at intervals afterwards for the each sample, by using Ostwald-viscometric technique [11]. Irradiation technique has been discussed in detailed elsewhere [5].

### Dilute solutions

Each of non-degradable and final degradable samples ( $M_i$  &  $M_t$ , respectively) was divided into ten parts. Equal amount of NaCl was added to each part with vigorous stirring. Then some extra double distilled water was added up to the required volume.

### Density and viscosity measurements

The measurements were taken as described elsewhere [12]. The accuracy of the density and viscosity measurements was  $\pm 0.001\%$  and  $\pm 0.015\%$ , respectively. In addition, measured values were expressed in terms of reduced ( $\eta_{red}$ ) and inherent ( $\eta_{inh}$ ) viscosities as follows [11, 13]:

$$\eta_r = t_{CMC} \times \rho_{CMC} / t_s \times \rho_s; \quad (1)$$

$$\eta_{sp} = \eta_r - 1; \quad (2)$$

$$\eta_{red} = \eta_{sp} / C_p \quad (3)$$

and

$$\eta_{inh} = \ln \eta_r / C_p \quad (4)$$

where  $t_{CMC}$  = the solution efflux time of dilute CMC salt solution,  $t_s$  = the solvent efflux time of  $0.01\text{M}$  salt solution,  $\rho_{CMC}$  = the solution density of dilute CMC salt solution,  $\rho_s$  = the solvent density of  $0.01\text{M}$  salt solution,  $\eta_{CMC}$  = the solution viscosity of dilute CMC salt solution,  $\eta_s$  = the solvent viscosity of  $0.01\text{M}$  salt solution,  $\eta_r$  = the relative solution viscosity of dilute CMC salt solution, and  $C_p$  = the concentration ( in mass per volume) of dilute CMC salt solution.

### Theoretical calculations

(i) values for relative average viscosity molar mass ( $\langle M_V \rangle_r$ ) were calculated according to Mark-Houwink equation [14,15]:

$$[\eta] = 8.1 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1} \langle M_V \rangle_r^{0.92} \quad (5)$$

where  $[\eta]$  = intrinsic viscosity and  $\langle M_V \rangle_r = \langle M_V \rangle / 1 \text{ g mol}^{-1}$ ,

(ii) hydrodynamic volume ( $V_h$ ), root-mean-square end-to-end distance ( $\langle r^2 \rangle^{1/2}$ ) and radius of gyration ( $\langle s^2 \rangle^{1/2}$ ) were calculated according to Einstein equation [16]:

$$V_h = (2/5) [\eta] \langle M_V \rangle / N_A \quad (6)$$

and Flory equation [17]:

$$[\eta] = \Phi \langle r^2 \rangle^{3/2} / \langle M_V \rangle, \quad (7)$$

$\Phi$  is Flory viscosity constant ( $2.1 \times 10^{23} \text{ mol}^{-1}$ ) [14],

and Debye expression [18]:

$$\langle s^2 \rangle^{1/2} = \langle r^2 \rangle^{1/2} / (6)^{1/2}, \text{ respectively,} \quad (8)$$

(iii) hydrodynamic expansion factor ( $\alpha$ ), unperturbed root-mean-square end-to-end distance ( $\langle r^2 \rangle_o^{1/2}$ ), unperturbed radius of gyration ( $\langle s^2 \rangle_o^{1/2}$ ) were calculated according to Flory-Fox relations [14, 17]:

$$[\eta] = 0.42 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \langle M_V \rangle_r^{1/2} \alpha^3 \quad (9)$$

and

$$\alpha = \langle r^2 \rangle^{1/2} / \langle r^2 \rangle_o^{1/2} = \langle s^2 \rangle^{1/2} / \langle s^2 \rangle_o^{1/2} \quad (10)$$

(iv) real values for number of UV-scission ( $S$ ) and degree of photodegradation ( $\beta$ ) were calculated as follows [1,4, 14]:

$$S = ([\eta]_i / [\eta]_f)^{1/0.92} - 1 \quad (11)$$

and

$$\beta = S / \langle DP \rangle; \quad (12)$$

$$\langle DP \rangle = n / 2 \quad (13)$$

and

$$n = 2 \langle M_V \rangle / M_u \quad (14)$$

where  $[\eta]_i$ ,  $[\eta]_f$  are the real initial and final intrinsic viscosities (non-irradiated and irradiated one), respectively;  $\langle DP \rangle$  is the average degree of polymerization,  $n$  is number of bonds and  $M_u$  is the molar mass of CMC repeating unit, respectively; while the ideal corresponding values were calculated as:

$$S_o = ([\eta]_{o(i)} / [\eta]_{o(f)})^{1/2} - 1 \quad (15)$$

$$\text{where } [\eta]_o = [\eta] / \alpha^3, \quad (16)$$

$[\eta]_o$  = ideal intrinsic viscosity;

and

$$\beta_o = S_o / \langle DP \rangle.$$

(17)

## Results and Discussion

The measured and calculated results are given in Figures (1-3) and Tables (1-4). The degradation curve of Figure 1 demonstrates the progress of UV scission on the chain of CMC in water. It suggests that the UV-irradiation had a very marked scission-in effect up to 270 min, whereas no more effect is observed after such exposure time [1-5].

Figures 2 and 3 show typical plots of density and reduced or reciprocal inherent viscosity values against concentration, respectively; all being increasing linearly over the dilute concentration range involved. On the other hand, the rate of increment in these values after UV-irradiation is less than in those before UV-irradiation. The linear plots of Figure 2 reflect the free volume reduction in an ideal dilute salt solution of CMC before and after UV irradiation [19,20]. Figure 3, also, reflects such reduction and, in addition, indicates the

absence of chains entanglement [19,21,22] for CMC in dilute salt solution. Thus both Figures (2 and 3) demonstrate the effect of solvation sheath which leads to an increase in the size of CMC molecule and, consequently, to an increase in the values of the mentioned viscosities, with increasing concentration [19].

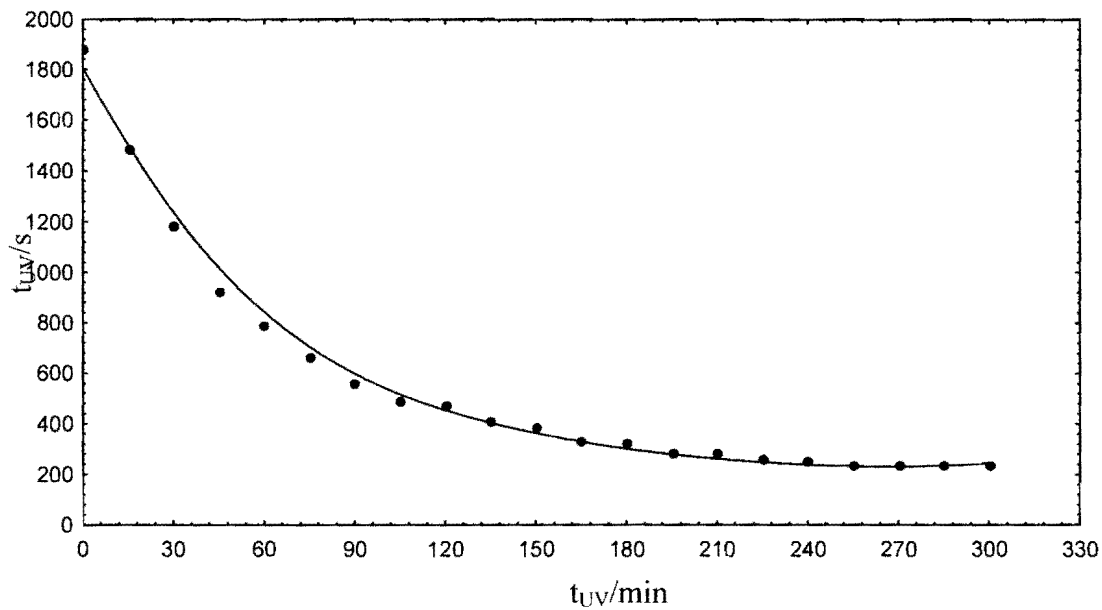


Figure 1: Efflux time changes for CMC in water with UV-exposure time at 25 °C

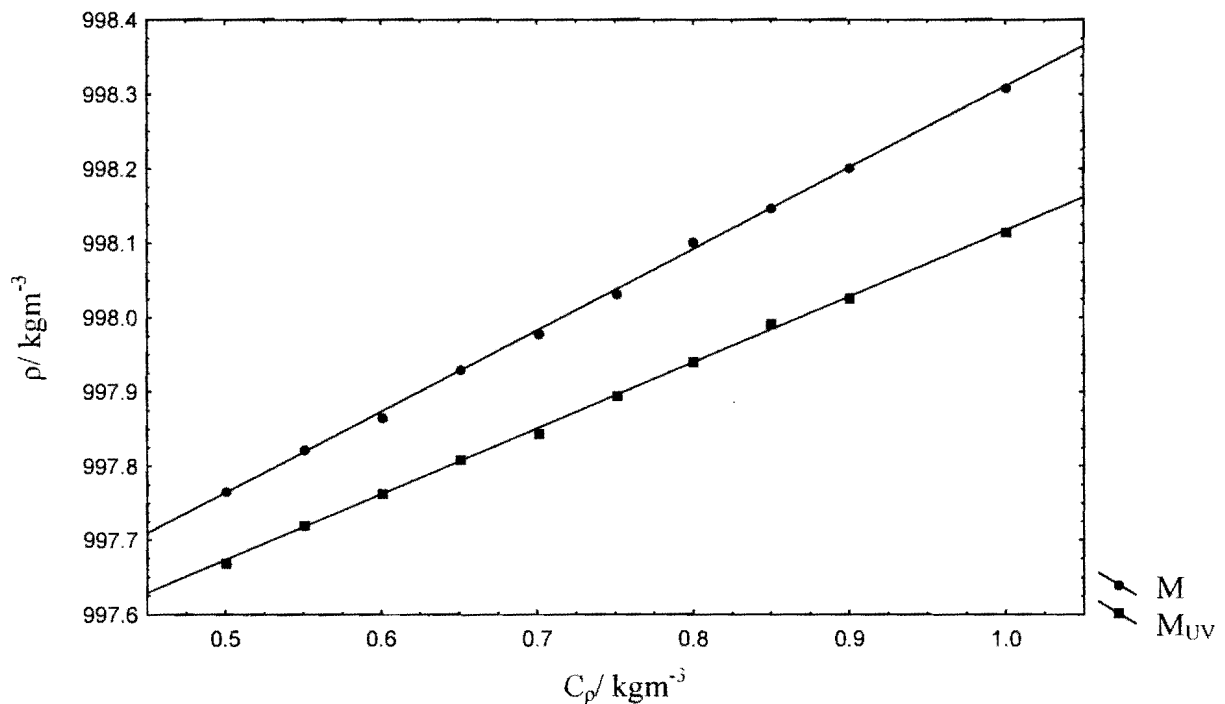
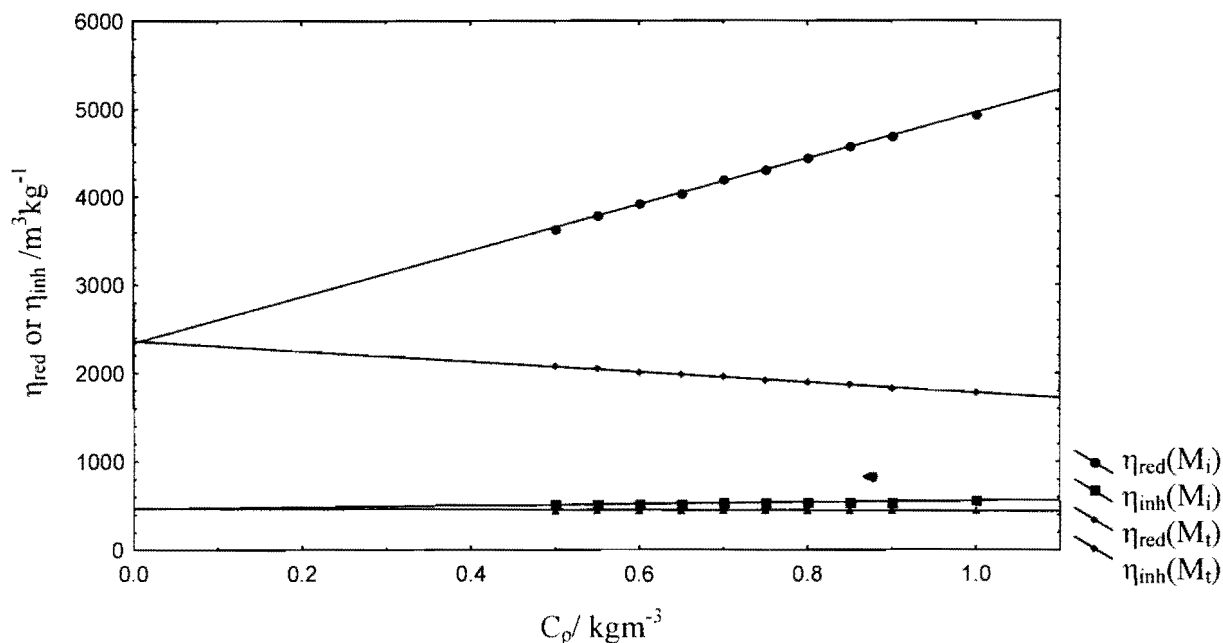


Figure 2: Linear increase of density with increasing concentration for dilute CMC salt solution before and after UV-irradiation at 25 °C



**Figure 3: Linear increase of reduced or reciprocal inherent viscosity with increasing concentration for dilute CMC salt solution before and after UV-irradiation at 25 °C**

**Table 1: Intrinsic viscosity and related parameters for CMC in salt solution before and after UV-irradiation at 25°C.**

Sample	$[\eta] / 10^{-3} \text{ m}^3 \text{ kg}^{-1}$	$k_b / 10^{-2}$	$k_k / 10^{-2}$	$\langle M_V \rangle_r$
$M_i$	2352.74	47.39	10.55	867241.65
$M_t$	469.73	41.62	11.70	150511.19

**Table 2 : Hydrodynamic volume and real chain dimensions for CMC in salt solution before and after UV-irradiation at 25°C.**

Sample	$V_h / 10^{-18} \text{ m}^3$	$\langle r^2 \rangle^{1/2} / 10^{-8} \text{ m}$	$\langle s^2 \rangle^{1/2} / 10^{-8} \text{ m}$
$M_i$	1.36	213.39	87.11
$M_t$	0.05	69.57	28.40

**Table 3: Expansion factor and ideal chain dimensions for CMC in salt solution before and after UV-irradiation at 25°C.**

Sample	$\alpha$	$\langle r^2 \rangle_0^{1/2} / 10^{-8} \text{ m}$	$\langle s^2 \rangle_0^{1/2} / 10^{-8} \text{ m}$
$M_i$	1.82	117.33	47.90
$M_t$	1.42	48.88	19.96

**Table 4: Scission and related parameters for CMC in salt solution before and after UV-irradiation at 25°C.**

Sample	S	$\beta / 10^{-2}$	$S_0$	$\beta_0 / 10^{-2}$
$M_i$	0.00	0.00	0.00	0.00
$M_t$	4.76	0.77	0.56	0.09

The intrinsic viscosity before and after UV-irradiation in Table 1 was each taken as the average ordinate intercept for the straight lines drawn through the two sets of points in Figure 3; their slopes are related to one another in accordance with the mutually related equations of Huggins form [23]:

$$\eta_{red} = [\eta] + k_h [\eta]^2 C_p \quad (18)$$

and Kraemer form [33]:

$$\ln \eta_r / C_p = [\eta] - k_k [\eta]^2 C_p \quad (19)$$

where  $k_h$  and  $k_k$  are the Huggins and Kraemer constants, respectively.

Consideration of results in Tables (1-3) shows that the values of perturbed and unperturbed intrinsic viscosity, chain dimension and their related parameters for CMC in dilute salt solution are greater than those of UV-irradiated one. This could be attributed to the marked scission effect on the polymer chain which is demonstrated in Table 4. Indeed Table 4, also, reveals the fact that the photodegradation effect on perturbed CMC is higher than the unperturbed one. This could be ascribed to the reduction in the osmotic swelling of CMC chain by the solvent-polymer interactions and, consequently, to the exclude volume effect due to the compact nature of the unperturbed polymer [25-28], as it appears in the higher value of CMC expansion coefficient, compared with the degradable one.

Further consideration of results in Tables (2-4) indicates that the polymer in dilute salt solution has a more extended configuration than the degradable one due to the greater solute – solvent interaction, since the chain dimensions in Tables 2 and 3 are a convenient index of the polymer configuration and of its domain in space [25-28]. This would accord with high values of Huggins and reciprocal Kraemer constants, Table 1, for CMC, compared with the degradable one. Moreover, each of these interaction coefficients reflects how far the viscosity of the system increases with increase of polymer concentration, which is due to the interaction of the neighbouring chains [12,23,24]. Thus for the CMC in dilute salt solution, the solute – solute contact is greater than for the degradable one and consequently, for irradiated CMC, the solute – solvent interaction is greater than the non-irradiated one [14,25-28].

## Conclusion

CMC in water undergoes chain scission in presence of ultraviolet radiation in air. The period of exposure time has considerable influence on the amount of scission and consequently on the length of CMC in water. Characterization of density and viscosity of the polymer in very dilute concentration domain before and after ultraviolet irradiation reveals the fact that UV-irradiation of CMC induces degradation which in turn decreases the mass, size, extension configuration, solute–solute contact and increase the solute-solvent interpretation.

## REFERENCES

- [1] Geuskens G. (1975). Photodegradation of Polymers. In: *Comprehensive Chemical Kinetics: Degradation of Polymers*, C. H. Bamford and C. F. Tipper (Eds.), Elsevier, Amsterdam, pp 333-424.
- [2] Rabek J. F. (1975). Oxidative Degradation of Polymers. In: *Comprehensive Chemical Kinetics: Degradation of Polymers*, C. H. Bamford and C. F. Tipper (Eds.), Elsevier, Amsterdam, pp 425-538.
- [3] McNeill I. C. (1992). Fundamental Aspects of Polymer Degradation. In: *Polymers in Conservation*, N. S. Allen, M. Edge and C. V. Horie (Eds.), Royal Society of Chemistry, Cambridge, pp 14-31.
- [4] Rabek J. F. (1996). *Photodegradation of Polymers: Physical Characteristics and Applications*, Springer, Berlin.
- [5] Sheltami R. M. F. (2003). *Photodegradation Induced Changes in Transport Properties of Dilute CMC Solutions*. M.Sc. Thesis, Garyounis University, Benghazi
- [6] Glass J. E. (1986) Structural Features Promoting Water Solubility in Carbohydrate Polymers. In: *Water-Soluble Polymers: Beauty with Performance*, J. E. Glass (Ed.), Advances in Chemistry Series 213, ACS, Washington, DC., pp 3-27.
- [7] Just E. K. and Majewicy T. G. (1988). Cellulose Ethers. In: *Encyclopedia of Polymer Science and Engineering*, N. Bikales (Ed.), John Wiley and Sons, Inc., New York, pp 226-269.
- [8] Fei B., Wach R. A., Mitomo H., Yoshii F. and Kume T. (2000). Hydrogel of Biodegradable Cellulose Derivatives I. Radiation Induced Crosslinking of CMC, *J. Appl. Polym. Sci.* **78**: 278-283.
- [9] Wach R. A., Mitomo H., Yoshii F. and Kume T. (2001). Hydrogel of Biodegradable Cellulose Derivatives II. Effect of Some Factors on Radiation, *J. Appl. Polym. Sci.* **81**: 3030-3037.
- [10] Wach R. A., Mitomo H., Kudoh H., Muroya Y., Kasumura Y. and Yoshi F. (2005). *Polysaccharides Derivatives Crosslinked by Ionizing Radiation*, Proceeding of the 8<sup>th</sup> Polymers for Advanced Technologies International Symposium, Budapest.
- [11] Kulicke W. M. (2004). *Viscosimetry of Polymers and Polyelectrolytes*, Springer, Berlin.
- [12] EL-Ashhab, F., Sheha, L., Zubeir, O., EL-Dali, A. and Eid, A. E. (2002). Viscosity and Related Properties of Dilute Aqueous Solution of MC Before and After Gamma Irradiation, *Egypt. J. Appl. Sci.* **17**: 62-71.
- [13] IUPAC Report (1952). On Nomenclature in the Field of Macromolecules, *J. Polym. Sci.* **8**: 257-277

- [14] Kurata M. and Tsunashima Y. (1999). Viscosity-Molecular Weight Relationship and Unperturbed Dimension of Linear Chain Molecules. In: *Polymer Handbook*, J. Brandrup, E. H. Immergut and E. A. Grulke (Eds.), John Wiley and Sons, Inc., New York, pp 265-266.
- [15] Houwink R. (1940). Cited in Physical Chemistry of Macromolecule, *J. Prakt. Chem.* **157**: 15.
- [16] Einstein A. (1906). Eine Neue Bestimmung der Molekuldimension, *Ann. Phys.* **19**: 289-306.
- [17] Flory P. J. and Fox T. G. (1951). Treatment of Intrinsic Viscosities, *J. Amer. Chem. Soc.* **73**: 1904 –1908.
- [18] Debye P. (1946). The Intrinsic Viscosity of Polymer Solutions, *J. Chem. Phys.* **14**:336-339.
- [19] Prigogine I. (with the collaboration of Bellemans, A. and Mathot, V.) (1957). *The Molecular Theory of Solutions*, Interscience Publishers, New York.
- [20] Bauer N. and Lewin S. Z. (1972). Determination of Density. In: *Physical Methods of Chemistry*, A. Weissberger and B. W. Rossiter (Eds.), Techniques of Chemistry, New York.
- [21] Bueche F. (1952). Viscosity, Self. Diffusion and Allied Effects in Solid Polymers, *J. Chem. Phys.* **20**: 1959-1964.
- [22] Doi M. and Edwards S. F. (1988). *The Theory of Polymer Dynamics*, Oxford University Press, New York.
- [23] Huggins M. L. (1942). The Viscosity of Dilute Solutions of Long-Chain Macromolecules IV. Dependence on Concentration, *J. Amer. Chem. Soc.* **64**: 2716-2718.
- [24] Kraemer E. O. (1938). Molecular Weight of Cellulose and Cellulose Derivatives. *Ind. Eng. Chem.* **30**: 1200-1203.
- [25] Flory P. J. (1949). The Configuration of Real Polymer Chains, *J. Chem. Phys.* **17**: 303-310.
- [26] Flory P. J. and Krigbaum W. R. (1950). Statistical Mechanics of Dilute Polymer Solutions, *J. Chem. Phys.* **18**: 1086-1094.
- [27] Flory P. J. (1969). *Statistical Mechanics of Chain Molecules*, Wiley-Interscience. New York.
- [28] Fujita H. (1997). *Polymer Solution: Studies in Polymer Science.* **9**, Elsevier Science Publishers B. V., Amsterdam.