Printed ISSN 1330–0008
Online ISSN 1333–9125
CD ISSN 1333–8390
CODEN FIZAE4

SUITABLE SOLVENT OF A NEW COPOLYMER AS A PRE-INVESTIGATION OF ITS STATIC LASER SCATTERING

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Received 27 December 2007; Revised manuscript received 17 October 2008
Accepted 22 October 2008 Online 28 January 2009

An interferometric method, Mach-Zehnder interferometer, is applied to determine both refractive index and refractive index increments (dn/dc) for a new copolymer material poly-(4-vinylphenol-co-2-hydroxethyl methacrylate), PVPh-HEM, in different solvents like methanol and dimethylformamide. The PVPh-HEM is solved in each solvent with different concentrations ranging from 0.004 to 0.010 g/ml. The light source we have used is the argon-ion laser with the wavelength of 488 nm. This work is carried out as a step for the determination of the average molecular weight of PVPh-HEM and its other related scattering parameters.

PACS numbers: 78.20.Ci, 36.20.-r UDC 532.77, 535.324

Keywords: poly-(4-vinylphenol-co-2-hydroxethyl methacrylate), refractive index, average molecular weight

1. Introduction

Its well known that most of modern applications use the polymers in many branches of sciences and life. Therefore, the physicists must play an important role in the investigations of physical properties of this kind of modern materials.

Polymers or macromolecules are high-molecular-weight compounds that are made up of repeating low-molecular-weight units called monomers. Polysaccharides, proteins and nucleic acids are natural polymers or biopolymers that are formed by plants and animals.

Since 1930, synthetic polymers have been produced industrially for use in manufacture of a wide variety of consumer products [1]. Therefore the need to study their physical properties such as refractive index, dielectric constant and polarizability.

Polymer solid electrolytes are materials of great technological interest because of their applications in solid-state batteries, capacitors and electrochromic devices.

Polymer electrolyte materials are characterized by an interesting conductivity behaviour that is highly dependent on the local structure and is influenced by the crystallization and ionic association [2].

The poly-(4-vinylphenol-co-2 hydroxethyl methacrylate), PVPh-HEM, is a new copolymer, its density is 1.2 g/ml at 25° C and its transition temperature is 700° C. This copolymer is used in electronics, solder resists, etching resists, presensitized printing plates, coatings and adhesives. The chemical formula of poly-(4-vinylphenol-co-2 hydroxethyl methacrylate) is shown in Fig. 1 [3]. It is used to improve the thermal, mechanical and spectroscopic properties of the other polymer materials like poly(ethylene oxide), PEO, to meet some new practical applications [2].

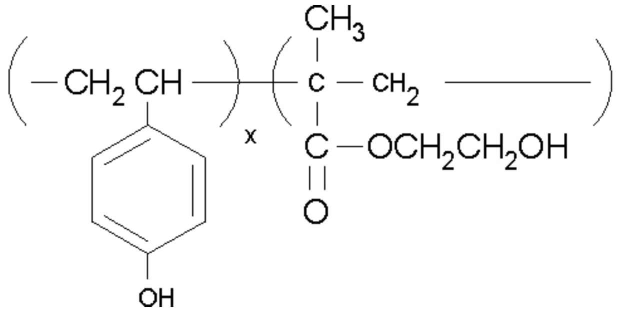

Fig. 1. The chemical formula of the poly-(4-vinylphenol-co-2-hydroxethyl methacrylate) copolymer.

2. Physical principles

The following fluctuation of concentration with light scattering turns out to be a great way to obtain thermodynamic information about polymeric and colloidal systems. Effectively, the tiny concentration fluctuations that occur spontaneously provide the same osmotic pressure information as a large, forced gradient imposed by a semi permeable membrane in a real osmometer. To unlock that information one needs a key: The specific refractive index increment, usually denoted $\mathrm{d}n/\mathrm{d}c$. The refractive index increment $\mathrm{d}n/\mathrm{d}c$ describes how much the refractive index of a solution varies for a given increment in the concentration, expressed as g/ml. The refractive index of a solution n can be expressed as follows in terms of the refractive index of the solvent n_0 and the concentration c (g/ml) of the polymer

$$\Delta n = n - n_0 = a_1 c + a_2 c^2 \,. \tag{1}$$

Hence

$$\Delta n / c = n - n_0 = a_1 + a_2 c \,. \tag{2}$$

In principle, the specific refractive index increment may depend on the concentration and is certainly influenced by the wavelength λ and temperature T. In the following account, $\mathrm{d}n/\mathrm{d}c$ will be understood to mean

$$\frac{\mathrm{d}n}{\mathrm{d}c} = \lim_{c\to 0} \left(\frac{\Delta n}{c}\right)_{\lambda,T} . \tag{3}$$

The value of $\mathrm{d}n/\mathrm{d}c$ should be obtained not as the slope of Δn versus c, but rather as the intercept, at $c = 0$ of the plot of $\Delta n/c$ versus c. Although such an extrapolation seems most reasonable, despite some speculative discussion on this score [4], no form of discontinuity or change of the slope has been detected, even at very high dilution.

The determination of absolute molecular weight precisely depends greatly on the accurate measurement of the change of refractive index with concentration because $\mathrm{d}n/\mathrm{d}c$ appears as a squared term in the Debye equation [5]

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w}\left[1 + \left(\frac{16\pi^2}{3\lambda^2}\right)\langle R_G^2\rangle \sin^2\left(\frac{\theta}{2}\right)\right] + 2A_2c + 3A_3c^2 + \ldots , \tag{4}$$

where c is the concentration, M_w the average molecular weight and K the optical constant for the particular scattering system given by

$$K = 2\pi^2 n_0^2 \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 \lambda_0^{-4} N_A^{-1} , \tag{5}$$

where n_0 is the refractive index of the solvent, $\mathrm{d}n/\mathrm{d}c$ the specific refractive index increment, λ_0 the wavelength in vacuum, N_A the Avogadro's number, $\lambda = \lambda_0/n_0$ the wavelength of light in the medium, $\langle R_G\rangle$ the mean square radius of gyration, which is independent of the particle shape at small angles, θ the angle of scattering and A_2, A_3 are the second and the third viral coefficients.

It is known that the refractive index increment does not vary dramatically (for a given solvent) from one polymer to another. For this reason, it is commonly assumed that it dos not vary at all as the given solvent's conditions are changed. Likewise, it is assumed that interactions between polymers do not affect the refractive index increment, even though one might expect otherwise [6].

When working with polymers, for the greatest accuracy, it is preferable to choose a solvent for which the quantity k is as large as possible. It is usually in the concentration range of 0.001 to 0.1 g/ml. Since for the practical range of concentrations this usually means a difference in the third decimal place of the refractive index, it is necessary to make measurements of refractive index with a high degree of accuracy. Measurements of the absolute values of the refractive index of the solutions and the calculations of the differences are thus ruled out for work of high precision. Therefore, direct measurements of the difference of refractive indices between the solvent and the solution performed [7,8,9].

3. Sample preparation

Measurements of scattering of light depend on the difference between the refractive index of polymer and its solvent. In general, they become more accurate with a larger refractive index increment. Therefore, the used solvents were chosen with great care to satisfy the previous conditions.

During the preparations of the solution, one must avoid its contamination (particles, grease and surfactants) since they all interact with the polymer. It is also an advantage to work in a clean room to manipulate the solution in a dust free environment.

During the experimental study, all solvents (Aldrich, co. & Merck) were used with initial and simple purification. All polymer solutions were filtered by using the usual conventional cellulose acetate membrane filters with 0.45 μm pore size in order to remove dust and multi-chain aggregates. The used poly-(4-vinylphenol-co-2-hydroxethyl methacrylate) copolymer of unknown molecular weight was imported from Aldrich (its catalog number is 47, 458-4).

4. Experiment

The aim is the determination of the specific refractive index increment $\mathrm{d}n/\mathrm{d}c$ of poly-(4-vinylphenol-co-2hydroxethyl methacrylate) solved in methanol and dimethylformamide (DMF) at room temperature. The measurements were made by using a single laser wavelength.

The full experimental details of the determination of the refractive index of liquids with the Mach-Zehnder interferometer (MZI) technique, with a total accuracy of 5.8×10^{-4} are given in Ref. [10].

The empty cell was placed in one arm of MZI. By rotating the sample about its vertical axis to change the angle of incidence ϕ of the laser beam, one can count the corresponding number of fringes N_1 which cross the field of view. When the angle of incidence ϕ is changed, the number of fringes is changed consequently to N_2. The range of the change of angle is from 7 to 22 degrees and the corresponding shift of fringes N is equal to the difference between N_1 and N_2 at the same recorded angle.

By applying the Snell's law of refraction and the relation between the angle of incidence and the number of fringes one can get the following formula [11 − 14]

$$n = \frac{(t - N\lambda)(1 - \cos\phi) + N^2\lambda^2/(2t)}{t(1 - \cos\phi) - N\lambda}\,, \tag{6}$$

where t is the thickness of the sample, ϕ the angle of incident laser beam, n the refractive index, N the number of interfere fringes corresponding to angle and λ the laser wavelength. The term $N^2\lambda^2/(2t)$ can be neglected as it is very small. By using the mathematical arrangement one gets

$$\frac{1}{\sin^2(\phi/2)} = \frac{2t(n-1)}{nN\lambda} + \frac{2}{n} \tag{7}$$

Equation (7) is suitable for graphical representation of results [15], where the refractive index results from the inverse of the intercept of the curve.

The difference in counts between the empty cell and the filled one at each cell rotation angle gives the path difference in solution. The graphical representation using Eq. (7) leads to the determination of the refractive index of the sample under investigation.

5. Results

5.1. Refractive index of methanol and dimethylformamide

The refractive indices of the chosen solvents, methanol and DMF were measured. The results are tabulated in Table 1 and represented graphically in Fig. 2. The results are in a good agreement with literature values [16].

TABLE 1. Values of refractive index of methanol and DMF solvents.

Solvent	Measured value $\lambda = 488$ nm		Literature value [16] $\lambda = 589$ nm	
	n	t (°C)	n	t (°C)
Methanol	1.32987	19	1.3288	20
DMF	1.43181	17	1.4305	20

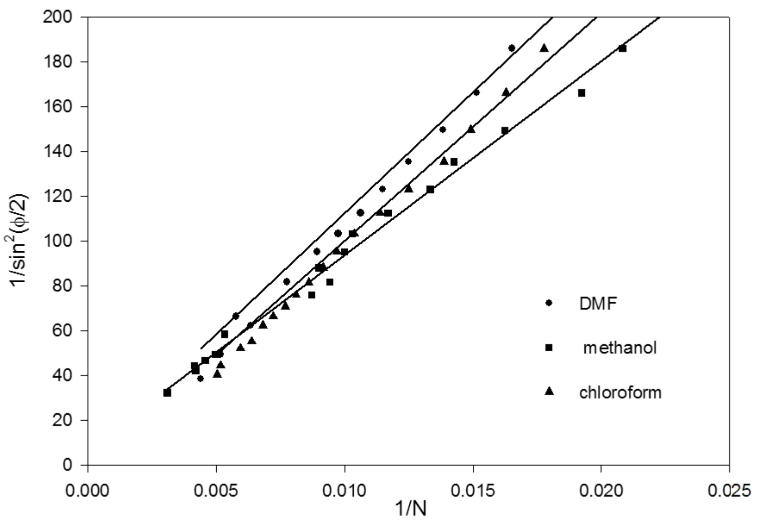

Fig. 2. Determination of refractive index of different solvents.

5.2. *Refractive index of different concentrations of PVPh-HEM*

Different concentrations of poly(4-vinylphenol-co-2 hydroxethyl methacrylate) in methanol and DMF in the range 0.004 to 0.01 g/ml were prepared. The refractive indices of these concentrations for the two solvents were measured by the same MZI method. The results are tabulated in Table 2 and are illustrated graphically in Fig. 3 for methanol and in Fig. 4 for DMF.

TABLE 2. Refractive index of poly-(4-vinylphenol-co-2 hydroxethyl methacrylate) solved in methanol and DMF at different concentrations at $\lambda = 488$ nm.

Concentration	Methanol		DMF	
(g/ml)	n	t (°C)	n	t (°C)
0.004	1.33175	23	1.43256	21
0.006	1.33204	23	1.43289	21
0.008	1.33248	23	1.43313	21
0.01	1.33283	23	1.43343	21

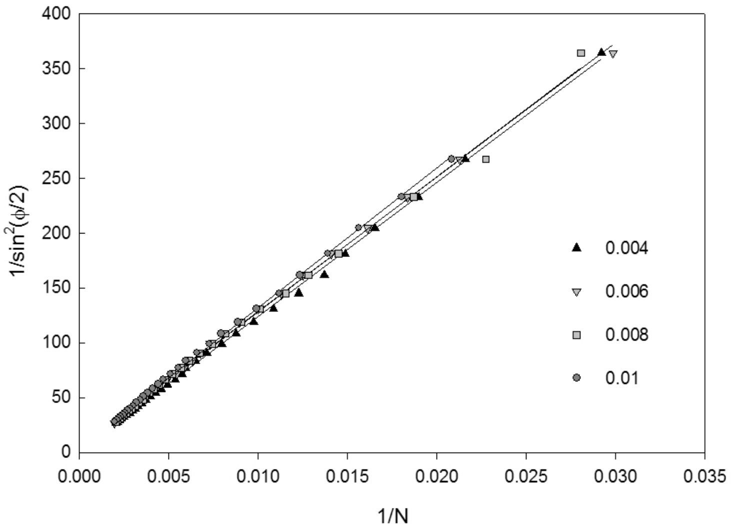

Fig. 3. Laser interferometer determination of refractive index of poly-(4-vinyle phenol-co-2 hydroxethyl methacrylate) solved in methanol at different concentrations c g/ml).

5.3. *Specific refractive index increment,* dn/dc, *of PVPh-HEM*

For both solvents, the change in the specific refractive index of the solution with respect to the concentration was measured. The value of dn/dc was obtained from

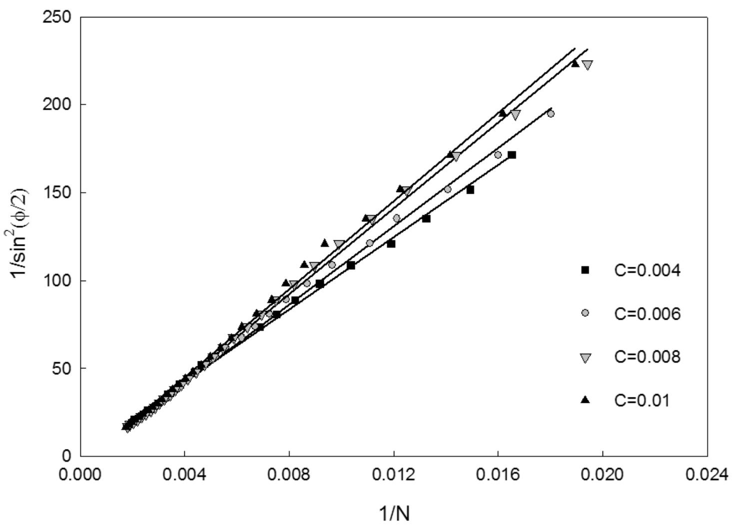

Fig. 4. Interferometer determination of refractive index of poly-(4-vinylephenol-co-2 hydroxethyl methacrylate) solved in DMF at different concentrations c g/ml).

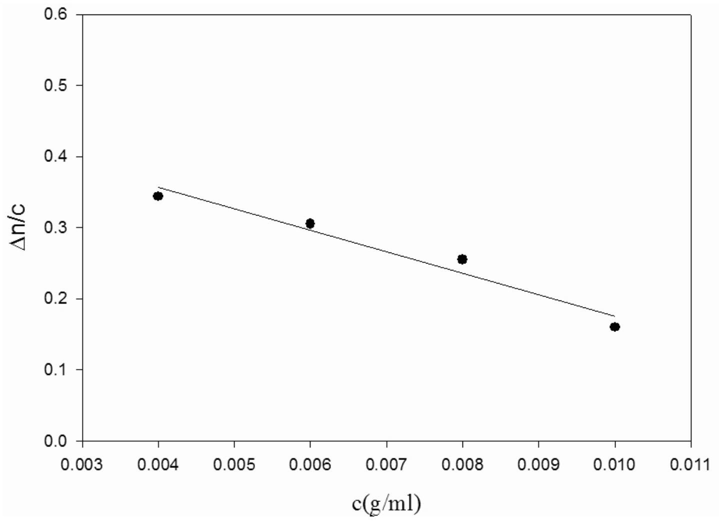

Fig. 5. Determination of the specific refractive index increment at zero concentration, $\mathrm{d}n/\mathrm{d}c = 0$*, of PVPh-HEM solved in methanol.*

the plot of $\Delta n/c$ against c, as shown in Fig. 5 for methanol and Fig. 6 for DMF. The results are summarized in Table 3. In all graphs the solid line indicates the best fit for each set of data obtained from the linear regression analysis.

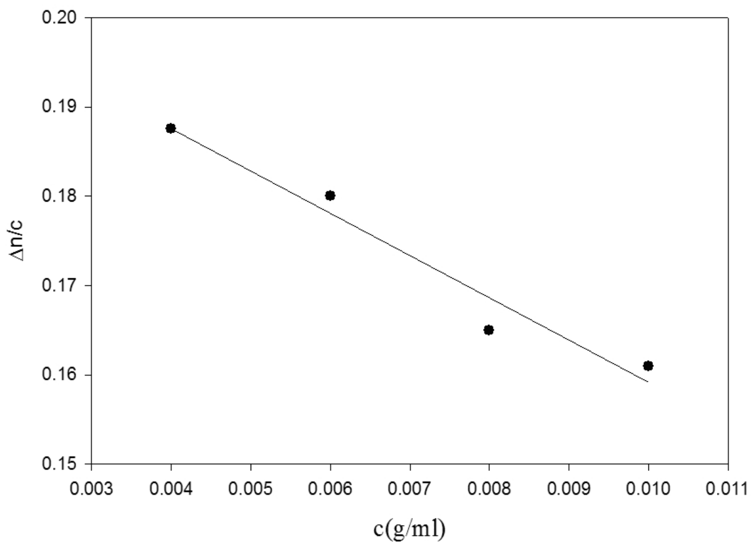

Fig. 6. Determination of the specific refractive index increment at zero concentration, $\mathrm{d}n/\mathrm{d}c = 0$*, of PVPh-HEM solved in DMF.*

TABLE 3. Refractive index increment of poly-(4-vinylphenol co-2 hydroxethyle methacrylate) solved in different solvents and measured at $\lambda = 488$ nm. *No previous data are known to the author.*

Solvent	$\mathrm{d}n/\mathrm{d}c$	t (°C)
Methanol	0.385	23
DMF	0.194	21

6. *Conclusion*

The first experimental determination of the refractive index of poly-(4-vinylphenol-co-2 hydroxethyl methacrylate) as a copolymer solved with different concentrations in methanol and DMF has been made with a high degree of accuracy. The refractive index increments of the copolymer were investigated as a pre-study for the laser scattering phenomena. It is shown that the refractive index increment $\mathrm{d}n/\mathrm{d}c$ in the case of methanol solution is larger than that for DMF solution. Therefore, the second virial coefficient A_2 will be high in the determination of the scattering parameters according to the Debye equation (4), as will appear in the following study. Also, the scattering intensity in the case of methanol will be larger than in the case of DMF.

References

[1] G. H. Schmidt, *Organic Chemistry*, Mosby-Year Book, Inc. (1996).

[2] A. Rocco, C. Bielschowsky and R. Pereira, Polymer **44** (2003) 361.

[3] www.Sigma-Aldrich.com.

[4] S. Lowey, J. Kucera and A. Holtzer, Mol. Biol. **7** (1963) 234.

[5] P. Debye, J. Phys. Colloid Chem. **51** (1947) 18.

[6] K. Hery and D. Norwood, *Determination of Refractive Index Increment*, College of Arts and Science, South Eastern Louisiana University (2002).

[7] G. Nikolic, M. Cokic and L. Ailic, J. Chem. Soc. **66** (2001) 397.

[8] B. El-Baradie, R. Ghazy, A. El-Shaer and F. El-Mekawey, Physica B **292** (2000) 208.

[9] R. Ghazy, A. El-Shaer, B. El-Baradie and F. El-Mekawey, Optics and Laser Technology **31** (1999) 335.

[10] R. Ghazy, Acta Physica Polonica A **95** (1999) 939.

[11] K. Betzler, A. Grone, N. Schmitl and O. Voigt, Rev. Sci. Instr. **59** (1988) 652.

[12] U. Schlarb and K. Betzler, Ferroelectrics **126** (1993) 39.

[13] B. Richerzhogen, Applied Optics **35**, 10 (1996) 1650.

[14] W. Demtröder, *Laser Spectroscopy*, 2nd Enlarged Edition, Springer (1995).

[15] M. Khashan and A. Nassif, J. Mod. Optics **36** (1989) 783.

[16] R. C. Weast, editor, *Handbook of Chemistry and Physics*, 59th ed., The Chemical Rubber Co. (1979) E-354, E-355.

POVOLJNO OTAPALO ZA NOV KOPOLIMER U PREDISTRAŽIVANJU NJEGOVOG STATIČKOG LASERSKOG RASPRŠENJA

Primijenili smo interferometrijsku metodu s Mach-Zehnderovim interferometrom za određivanje indeksa loma i porasta indeksa loma ($\mathrm{d}n/\mathrm{d}c$) za novu kopolimersku tvar, poli-(4-vinilphenol-co-2-hidroksetil metacrilat). Taj se kopolimer otapao u svakom otapalu s različitim koncentracijama između 0.004 i 0.010 g/ml. Rabili smo argon-ionski laser valne duljine 488 nm kao izvor svjetla. Ovaj je rad predistraživanje za određivanje prosječne molekulske težine tog kopolimera i odnosnih parametara raspršenja.