

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/255778426>

Scattering from polyelectrolyte solutions

ARTICLE *in* JOURNAL OF THE CHEMICAL SOCIETY FARADAY TRANSACTIONS 1 · JANUARY 1988

Impact Factor: 4.2 · DOI: 10.1039/F19888401563

CITATIONS

15

READS

3

3 AUTHORS, INCLUDING:



Malcolm J. Grimson

University of Auckland

97 PUBLICATIONS 1,049 CITATIONS

SEE PROFILE



Mustapha Benmouna

Abou Bakr Belkaid University of Tlemcen

120 PUBLICATIONS 1,153 CITATIONS

SEE PROFILE

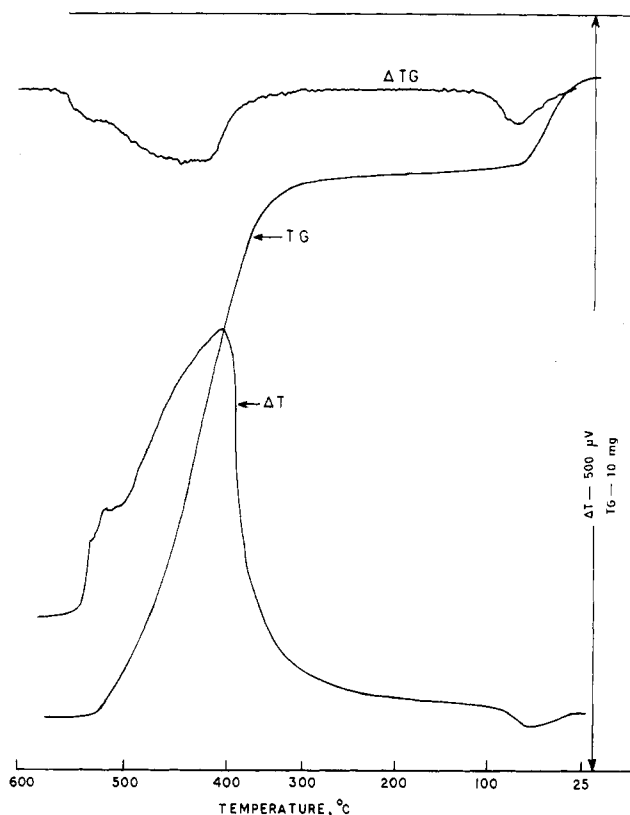


Figure 1. Thermograms of biphenol- CBr_4 condensate.

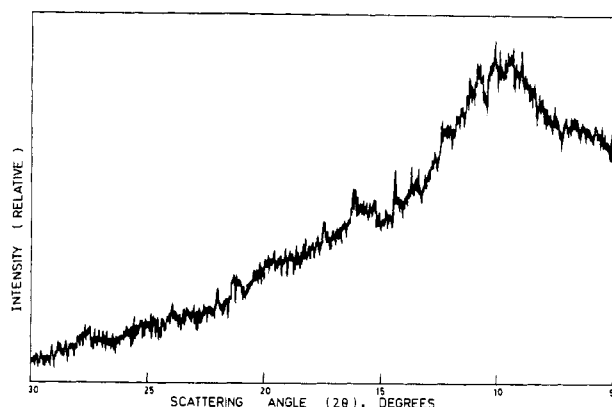


Figure 2. X-ray diffractogram of biphenol- CBr_4 condensate.

groups which, due to four electronegative oxygen atoms, are susceptible to facile oxidative degradation.

X-ray Diffraction. An X-ray diffractogram of the polymer was recorded with $\text{Mo K}\alpha$ 0.071-nm radiation. A typical X-ray diffractogram is illustrated in Figure 2, which has the characteristics of amorphous materials. There are, however, some peaks of low intensity that are not well resolved.

The apparent absence of any well-defined peaks in the diffractogram may be attributed to either of two reasons. First, the polymer was itself obtained in an amorphous form. This is quite likely in view of the facts that the condensation may be incomplete in regard to the formation of closed tetrahedral network and that there may be rotation around the carbon-oxygen-aryl bonds, leading to a large deformation in the structure. The latter could have been minimized by prolonged annealing at a suitable temperature to bring about uniformity in the network. However, in view of the poor thermal stability of the polymer even at lower temperature, (vide thermal stability) no improvement in the diffractogram was observed.

Second, the regular uniform network might have led to a large unit cell dimension and hence to too low an angle of diffraction maximum to be identified in the diffractogram. With the assumption of a perfectly ordered diamond cubic structure of the polymer, a large distance of 1.08 nm for the C-R-C linkages, and a low $\text{Mo K}\alpha$ radiation wavelength of 0.071 nm, the scattering angle (2θ) for the first-order diffraction for a diamond cubic lattice parameter of 2.488 nm works out to be only about 0.2° , which is too low to be detected in the diffractogram.

It, therefore, remains unresolved, at least from the diffraction pattern, as to whether the polymer is really crystalline.

Concluding Remarks

The proposed scheme of synthesis of a highly cross-linked ordered polymer appears to be applicable in the case of condensation between CBr_4 and disodium biphenolate, although the optimum conditions and the mode of carrying out the reaction are subject to variation depending upon the physical characteristics and reactivity of the component reactants. In the case of CBr_4 -biphenol condensate, many of the predicted properties like hardness, solubility characteristics, porosity, and pore size distribution have been attained. However, an ordered structure and high degree of crystallinity in the polymer could not be established unambiguously, and the prediction regarding thermal stability has been totally belied. It is expected that the ambiguity regarding an ordered structure and high degree of crystallinity of the cross-linked polymers can be resolved, and high thermal stability can be ensured by proper choice of the component reactants on the basis of their structures and reactivity. Further investigation in this direction is in progress.

Acknowledgment. We are thankful to Prof. S. K. Palit, Department of Chemistry, IIT, Kharagpur, India, for providing laboratory facilities, and to the colleagues of Materials Science Centre and in the Departments of Chemistry, Physics and Metallurgical Engineering, for fruitful discussions and analytical assistance.

Registry No. (4,4'- $\text{HOC}_6\text{H}_4\text{C}_6\text{H}_4\text{OH}\cdot 2\text{Na}$)(CBr_4) (copolymer), 106989-10-0.

References and Notes

- (1) Sober, H. A.; Peterson, E. A. *J. Am. Chem. Soc.* **1954**, *76*, 1711.
- (2) Abrams, I. M. *Ind. Eng. Chem.*, **1956**, *48*, 1469.
- (3) Meitzner, E. F.; Oline, J. A. French Patent 1 237 342, 1960.
- (4) Horvath, C. G.; Preis, B. A.; Lipsky, S. R. *Anal. Chem.* **1969**, *41*(10), 1227.
- (5) Morris, L. R. U.S. Patent 2 875 169, 1959.
- (6) Calmon, C. *J. Am. Water Works Assoc.* **1961**, *73*, 652.
- (7) Feeny, E. C. *Ion Exchange for Pollution Control* Calmon, C., Gold, H., Eds.; CRC Press, Boca Raton, FL; 1977; Vol. 2, Chapter 4.
- (8) Baker, B.; Davies, V. R.; and Yarnell, P. A. *Proc. Annu. Int. Water Conf.*, **38th** 1977, 259.
- (9) Kunin, R.; Preuss, A. F. *Ind. Eng. Chem., Prod. Res. Dev.* **1964**, *3*, 304.
- (10) Akzo Chemie (Holland), Bulletin.

Scattering from Polyelectrolyte Solutions

M. BENMOUNA[†] and M. J. GRIMSON*

AFRC Institute of Food Research, Norwich Laboratory, Norwich NR4 7UA, U.K. Received September 8, 1986

Benmouna et al.¹ have proposed a model for the scattering intensity from a dilute solution of charged macro-

[†] Permanent address: Department of Physics, Institute of Sciences, Tlemcen BP 119, Algeria.

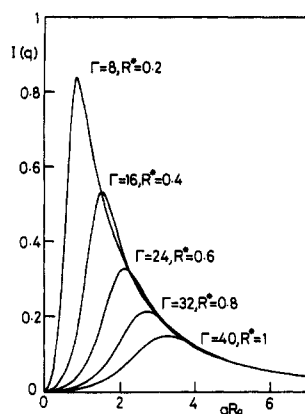


Figure 1. The scattering intensity (in arbitrary units) from a solution of polyelectrolyte chains in the form of Gaussian coils (with radius of gyration R_g) for different chain concentrations. The polyion charge is fixed with $\Gamma/R^* = 40$, and curves labeled by smaller Γ (or lower R^*) values correspond to more dilute solutions.

molecules. In this Note we present a generalization of this model that is, in principle, applicable to solutions of both spherical and rodlike polyelectrolyte chains at any concentration.

The scattering intensity $I(q)$ for a one-component system may be written

$$I(q) \propto P(q)S(q) \quad (1)$$

where $P(q)$ is the intrachain structure factor or form factor, $S(q)$ is the interchain structure factor, and the wavevector $q = (4\pi\lambda^{-1}) \sin(\theta/2)$ (λ being the wavelength of the incident radiation and θ the scattering angle). The structure factor may also be expressed in terms of the Fourier transform of the direct correlation function $C(q)$, which is defined by

$$S(q) = (1 - nC(q))^{-1} \quad (2)$$

where n is the number density of chains.² The present model consists of using the single-contact approximation³ to express $C(q)$ as a product of the form factor $P(q)$ and an interchain monomer-monomer interaction factor, which for uncharged macromolecules is known as the excluded volume parameter ν .⁴ However, for polyelectrolytes the range of interaction may be large due to the screened Coulomb interaction between charged monomers and ν becomes q -dependent. This represents a direct correlation between monomers on different chains which is denoted $C_m(q)$ and allows us to write

$$C(q) = C_m(q)P(q) \quad (3)$$

Hence we find from eq 1-3

$$I(q) \propto \frac{P(q)}{1 - nC_m(q)P(q)} \quad (4)$$

In the absence of added salt, when screening effects are small, the effective monomer-monomer direct correlation function $C_m(q)$ should be well represented by a one-component plasma (OCP) for all but very small wavevectors,⁵ the OCP being a one-component fluid of charged point particles interacting through an unscreened Coulomb potential where the counterions form a uniform neutralizing background.⁶

To illustrate this result, Figure 1 shows the scattering intensity for a solution of polyelectrolyte chains in the form of Gaussian coils where a Debye function may be used for $P(q)$ with

$$P(q) = 2u^{-2} (\exp(-u) + u - 1), \quad u^{1/2} = qR_g \quad (5)$$

and R_g is the radius of gyration of the coil.⁷ $I(q)$ is plotted for several values of the OCP coupling constant Γ^6 and ratio $R^* = R_g/a$ such that Γ/R^* is fixed ($a = (3/4\pi n)^{1/3}$ is the ion sphere radius for the polyion and typically $R^* \lesssim 1$). This corresponds to variations in the number density n for fixed values of the polyion charge, with smaller Γ (or lower R^*) values representing more dilute solutions. Figure 1 reproduces correctly the qualitative behavior of the experimental data reported by Nierlich et al.⁸ and Matsuoka et al.⁹ for the scattering intensity as a function of polyelectrolyte concentration for both biopolymers and synthetic polyelectrolytes.

It is relatively simple to fit the experimental and theoretical results by adjusting the apparent charge on the polyion, which is unknown due to the counterion condensation that may occur in such systems, and using an appropriate choice for the form factor $P(q)$.

The unphysical feature of Figure 1 occurs in the $q \rightarrow 0$ limit, when the OCP model requires $S(q) \rightarrow 0$ as $q \rightarrow 0$.⁶ However this feature is removed by the inclusion of screening effects from the counterions, which in such systems represents a small perturbation and affects the scattering at only very small wavevectors.⁵

A more elaborate study of this model along with its generalization to multicomponent systems is in progress and will be reported later.

Acknowledgment. M.B. is grateful to the Institute of Food Research and the University of East Anglia for their hospitality and to the AFRC for financial support through the Underwood Fund during the course of this work.

References and Notes

- (1) Benmouna, M.; Weill, G.; Benoit, H.; Akcasu, Z. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 1679.
- (2) Hansen, J.-P.; McDonald, J. R. *Theory of Simple Liquids*; Academic: London, 1976.
- (3) Zimm, B. H. *J. Chem. Phys.* **1946**, *14*, 164.
- (4) Benoit, H.; Benmouna, M. *Macromolecules* **1984**, *17*, 535.
- (5) Grimsom, M. J. *J. Chem. Phys.* **1983**, *79*, 5070.
- (6) Singh, H. B. *J. Stat. Phys.* **1983**, *33*, 371.
- (7) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (8) Nierlich, M. et al. *J. Phys. (Les Ulis, Fr.)* **1979**, *40*, 701.
- (9) Matsuoka, H. et al. *J. Chem. Phys.* **1985**, *83*, 378.

Phase Transitions in Cross-Linked Gels of Natural Polymers

TAKAYUKI AMIYA[†] and TOYOICHI TANAKA*

Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Received October 20, 1986

Some synthetic polymer gels were reported to undergo discontinuous volume phase transitions in response to infinitesimal changes in temperature,¹ solvent composition,²⁻⁵ pH,⁶ ionic composition,⁶ or by application of a small electric field across the gel.⁷ It has also been suggested theoretically that the phenomena are similar to the gas-liquid phase transition, where the reversible volume changes up to a couple of thousand times have been observed upon temperature change.² It has further been shown theoretically that for a gel to undergo a discontin-

[†]Permanent address: Wakayama Research Laboratories, Kao Corp., Wakayama 640, Japan.