On the Macromolecular Structure and Molecular Accessibility of Swollen Microporous Resins: A Combined ESR–ISEC Approach

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Abstract: A number of fairly hydrophilic microporous poly{*N,N*-dimethylacrylamide–methylenebisacrylamide} resins (cross-linking degree from 1 to 8%) have been examined with two conceptually and experimentally quite independent techniques that are able to provide information on the macromolecular structure and chemical accessibility of these materials in the swollen state. Electron spin resonance spectroscopy (ESR) and inverse steric exclusion chromatography (ISEC) gave quite consistent results in water, which are interpreted on the basis of a physico-mathematical model that fits the experimental data nicely. The resulting equation appears as a promising tool in the design of macromolecular materials for chemical and catalytic applications.

1. Introduction

"Microporous" [1] polymer supports represent a very extensive and articulated class of reactive and nonreactive materials which play important roles in fundamental technologies. The best-known materials are ion exchange resins, which are used not only in various water-treatment processes but also as catalysts. Microporous supports are employed in a number of biotechnological applications, ranging from potentialities[2] to industrial achievements.[3–6] In fact, microporous macromolecular matrices (gels) are currently utilized on an industrial scale as enzyme supports in biocatalyzed processes, such as the syntheses of aspartic and fumaric acids (Tanabe Seiyaky),[7] lactase-free milk, and 6-aminopenicillanic acid (Snamprogetti),[7] and for the conversion of acrylonitrile into acrylamide (ca. 10 000 tons/year).[5] Microporous resins are extensively used as stationary phases in chromatographic applications[6] and in the so-called "solid-phase polypeptide synthesis",[8] for which Merrifield was awarded the Nobel prize in 1984. Finally, a catalyst (Bayer K 6333) based on a microporous bifunctional resin is currently being used in a number of installations worldwide for the extensive removal (down to 10 ppb) of oxygen from water to be used in power plants.[9]

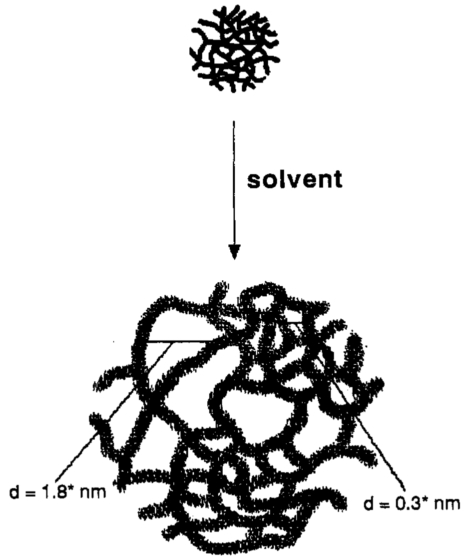

Figure 1. Schematic representation of the swelling process of a microporous resin (average distances between chains of lightly cross-linked poly(dimethylacrylamide) resins are shown).

All of these applications are performed under solid–liquid conditions, in which the resin is swollen by the liquid medium[1] (Figure 1). Swelling implies the development of a certain degree of microporosity within the polymer network, which is not present in the dry state. The structure of these materials in the swollen state can be described as a three-dimensional system of "meshes", which results from the entangling of cross-linked polymer chains. In view of the intrinsically inhomogeneous distribution[1] of the polymer chain concentration[10] in microporous resins, the actual size of the resulting meshes (in a given swelling medium) cannot be defined for a given polymer network, which turns out to be in fact characterized by a size distribution pattern. The intrinsic inhomogeneity is unavoidable and is the consequence of the kinetics of the polymerization reaction.[1]

In all the above mentioned applications, the functional capabilities of microporous supports are chiefly conditioned by

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(1) Guyot, A. In *Synthesis and Separations Using Functional Polymers*; Sherrington, D. C., Hodge, P., Eds.; Wiley: New York, 1988; p 1. Guyot, A. *Pure Appl. Chem.* **1988**, *60*, 365.

(2) Chibata, I.; Tosa, T.; Sato, T. *J. Mol. Catal.* **1986**, *37*, 1.

(3) Hoelderlich, W. F. In *New Frontiers in Catalysis*; Guczi, L., Solymosi, F., Tétényi, P., Eds.; Elsevier: Amsterdam, 1993; p 127.

(4) Rabo, J. *Ibid.* p 1.

(5) Watanabe, J. *J. Soc. Org. Synth. Chem.* **1988**, 46.

(6) Arshady, R. *Adv. Mater.* **1991**, *3*, 182 and references therein.

(7) Cooney, C. L. *Science* **1983**, *219*, 728.

(8) Merrifield, R. B. *Makromol. Chem., Macromol. Symp.* **1988**, *19*, 31.

(9) Wagner, R.; Lange, P. M. *Erdoel, Erdgas, Kohle* **1989**, *105*, 414.

(10) Jeřàbek, K. *Anal. Chem.* **1985**, *57*, 1598.

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their molecular accessibility, namely, by their ability to be crossed by reagents and products moving to and from the reaction sites. In this connection, chemical intuition predicts that the translational mobility of these species is controlled by the average polymer chain concentration, and, considering that the cavities defined by the polymer chains are nanometric in size, physics tells us that the diffusion rate of the molecules is decreased by (at least) a microviscosity effect.[11]

On these grounds, it appears quite obvious that any rational application of these materials ought to be preceded by a careful examination of their three-dimensional macromolecular structures and of their molecular accessibilities. A number of techniques appear to have been evaluated for this purpose, including scattering techniques,[12] thermoporometry,[13] UV and fluorescence probe studies,[14-16] ^{13}C-NMR relaxation processes,[17] ESR of paramagnetic "spin labels" and "spin probes",[18-21] and inverse steric exclusion chromatography (ISEC).[10] Although all these methodologies have looked at various useful facets of the macromolecular structure of these materials, it seems fair to state that an appropriate combination of two or more such techniques would represent a valuable conceptual and operational approach to the characterization of swollen microporous resins. We describe in this paper a promising example of this novel strategy aimed at correlating the information that stems from a rather complex and time-demanding (although highly informative) technique, like ISEC, with that offered by simple ESR measurements performed on paramagnetic probes confined to the examined swollen resin.[19] The two techniques provide quite independent and complementary information on the investigated matrices.

2. Results and Discusssion

ISEC, a version of the well-known size exclusion chromatography, provides information on the microporous structure of a swollen polymer matrix through mathematical processing of elution data of standard solutes possessing known molecular sizes. The data are obtained from liquid chromatography experiments in which the swollen gel to be characterized is used as the stationary phase. The mathematical treatment is based on the Ogston model,[22] which depicts the polymer chains as cylindrical, randomly oriented rigid rods. It is convenient to express the resulting information in terms of volume distribution of the discrete fractions of swollen polymer mass with different polymer chain density (nm/nm^3 = nm^{-2}). The volumes of individual fractions are referred to the unit mass of dry material and thus are expressed in cm^3/g.

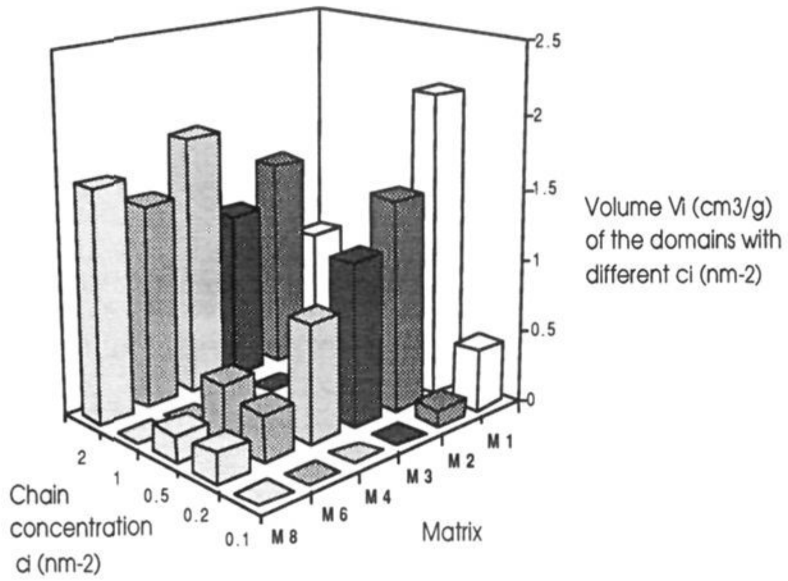

Figure 2. ISEC pattern displayed by matrices **M1**−**M8** in water, at 295 K.

Table 1. Average Chain Concentrations and Calculated and Experimental Values of the Total Swollen Gel Volumes of Matrices **M1**−**M8**

matrix	c_c[a]	total swollen gel vol[b]	
		calcd	exptl
M1	0.64	3.39	3.76
M2	1.06	3.06	3.21
M3	1.05	2.60	2.88
M4	1.36	2.63	2.60
M6	1.44	2.13	2.28
M8	1.69	1.99	2.02

[a] $c_c = \sum V_i c_i / \sum V_i$ = average chain concentration (nm^{-2}). [b] In cm^3/g.

ESR spectra of probes rotating in a solvent confined inside nanometric cavities provide information on (i) the accessibility of the material to the given probe molecule and on (ii) the rotational mobility (therefore indirectly on the translational mobility) of the probe as conditioned either by the microviscosity of the solvent inside the micropores or by possible interactions of the paramagnetic reporter with the polymer chains.[23] As the viscosity of a solvent dispersed in nanometric cavities is known to increase with the decrease of their relative sizes,[11] a possible physical relationship between the outputs of ISEC and ESR is feasible.

We tested our working hypothesis on a set of *ad hoc* designed microporous poly{*N*,*N*-dimethylacrylamide−methylenebisacrylamide} resins in which the cross-linking degree ranged from 1 to 8%[24] (resins **M1**−**M8**). A single batch of the various resins was analyzed by both ISEC and ESR spectroscopy.

The morphology of the investigated polymers in the swollen state is assumed to be composed of five discrete fractions of polymer mass, characterized by polymer chain density 0.1, 0.2, 0.5, 1.0, and 2.0 nm^{-2}, respectively.[25] The pattern of volume distribution among the five fractions displayed by resins **M1**−**M8**, as obtained from ISEC, is depicted in Figure 2.

The overall picture is very informative. Resins **M8** and **M6** appear to be dominated by high chain density (2 nm^{-2}) domains, while resins **M1**−**M4** appear to be rather bidisperse materials. In these resins the total gel volume turns out to be divided mainly into 0.2 and 2.0 nm^{-2} microporous domains, with the 0.2 nm^{-2} domains becoming gradually dominating as the cross-linking degree decreases from 8 to 1%.

It should be appreciated that the total swollen gel volume per gram of dry resin, obtained from the ISEC-derived morphology model as the sum of the volumes referring to individual chain densities, fits remarkably well with the experimental value for all the investigated matrices (Table 1). The experimental values are obtained upon dividing the difference between the

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[11] Nimtz, G. In *Correlations and Connectivity*; Stanley, H. E., Ostrowsky, N., Eds; NATO ASI Series 118; Kluwer: Dordrecht, 1990; p 225.

[12] Hecht, A. M.; Duplessix, R.; Geissler, E. *Macromolecules* **1985**, *18*, 2167.

[13] Brun, M.; Quinson, J. F.; Blanc, R.; Negre, M.; Spitz, R.; Bartholin, M. *Makromol. Chem.* **1981**, *182*, 873.

[14] Velasquez, D. L.; Galin, J. C. *Macromolecules* **1986**, *19*, 1096.

[15] Shea, K. J.; Sasaki, D. Y.; Stoddard, G. J. *Macromolecules* **1989**, *22*, 1722.

[16] Jeřàbek, K.; Shea, K. J.; Sasaki, D. Y.; Stoddard, G. J. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 605.

[17] Ford, W. T.; Perigasany, M.; Spivey, H. O. *Macromolecules* **1984**, *17*, 2881.

[18] Rex, G. C.; Schlick, S. *J. Phys. Chem.* **1985**, *89*, 3598.

[19] Regen, S. L. *Macromolecules* **1975**, *8*, 689.

[20] Watanabe, T.; Yahagi, T.; Fujiwara, S. *J. Am. Chem. Soc.* **1980**, *102*, 5187.

[21] Rockenbauer, A.; Lindgren, M.; Tabata, M.; Yang, W. *Eur. Polym. J.* **1993**, *29*, 945.

[22] Ogston, A. G. *Trans. Faraday Soc.* **1958**, *54*, 1754.

[23] Windle, J. J.; Scherrer, R. *Magn. Reson. Chem.* **1992**, *30*, 927.

[24] Palma, G.; Lora, S. To be published.

[25] The number of fractions in which the polymer is supposed to be divided cannot exceed the number of independently eluted probes.

Table 2. Rotational Correlation Times and Activation Energies (E_a) of TEMPONE Dissolved in Water Confined inside Matrices **M1–M8**

matrix	τ at 295 K (ps)	E_a (kJ/mol)
bulk soln	54	25
M1	138	25
M2	183	27
M3	206	28
M4	285	24
M6	343	25
M8	478	24

volume of the chromatographic column and the dead volume (the elution volume of a solute so large as to be completely excluded from the swollen gel) by the mass of the dry polymer sample employed as the stationary phase. The volume-weighted average polymer chain concentrations are also reported in Table 1.

For ESR experiments, each sample was analyzed after soaking the resin with a 10^{-4} M aqueous solution of the spin probe TEMPONE (2,2,6,6-tetramethyl-4-oxo-1-oxypiperidine). The relevant spectra of aqueous solutions of TEMPONE dispersed inside matrices **M1–M8** reveal that the probe experiences a relatively good rotational mobility (uncomplicated spectra) in all cases. Moreover, the rotational mobility is seen to decrease considerably on going from **M1** to **M8**, as revealed by the marked broadening of the high-field spectral peak.[26]

The effect of the temperature on the spectral pattern and τ values does confirm the uncomplicated behavior of the probe inside matrices **M1–M8** (Table 2). In fact, ln τ versus $1/T$ plots produce parallel straight lines. Thus, for all the matrices the activation energy has practically the same value, typical of a microviscosity-controlled phenomenon.[27]

The ESR results lead to the following conclusions: (i) TEMPONE, a molecule of substantial size (ca. 0.2 nm^3), easily gains access to the microporous domains in moderately cross-linked poly{dimethylacrylamide} matrices swollen in water; (ii) the probe rotates rather freely at room temperature inside the nanometer-sized cavities of these materials; (iii) the increasing rotational hindrance experienced by TEMPONE in more and more cross-linked matrices reflects what is essentially a microviscosity phenomenon; (iv) the increase of viscosity is paralleled by an increase of polymer chain density, which, in turn, corresponds to a decrease of the size of the reticular cavities. The expected consequence of these conclusions is a relationship, at least qualitative, between τ and c_c.

Actually, Figure 3 reveals a remarkably linear relationship between ln τ and c_c in a large temperature range (265–305 K):

$$\ln \tau = \ln \tau_0 + Kc_c \tag{1}$$

where K is a temperature-independent constant. Remarkably, the value of τ_0, extrapolated to $c_c = 0$, is very close to the experimental value observed for bulk water at each investigated temperature.

3. The Physico-Mathematical Model

We assume that a swollen microporous matrix can be considered as a semidilute polymer solution.[1] Thus, in analogy with the equation for the viscosity of concentrated suspensions of fibers recommended by Nicodemo and Nicolais,[28] we propose that the viscosity η inside swollen microporous matrices is given by

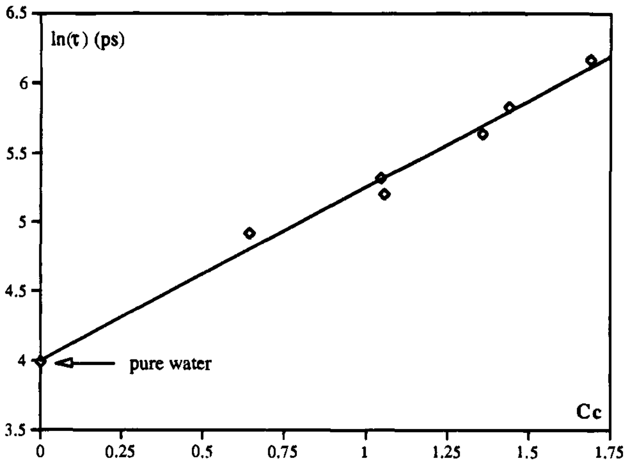

Figure 3. Experimental relationship between rotational correlation time of TEMPONE dissolved in water confined inside matrices **M1–M8** and their weighted average chain density (295 K).

$$\eta = \eta_0 \exp(\nu\Phi) \tag{2}$$

where Φ is the volume fraction of polymer chains, η_0 is the viscosity of the pure solvent, and ν is a convenient parameter.

If we refer to a resin according to the Ogston model,[22] with polymer chains considered as cylindrical rods of radius r_c and featured by a *single* chain density c, Φ is

$$\Phi = V_{\mathrm{polymer}}/V_{\mathrm{total}} = \pi r_c^2 L/V_{\mathrm{total}} = \pi r_c^2 c \tag{3}$$

where L is the total length of the polymer chains. From eqs 2 and 3 we deduce

$$\eta = \eta_0 \exp(\nu\pi r_c^2 c) \tag{4}$$

From the combination of the Stokes–Einstein equation with eq 4 we get

$$\tau = (4\pi a^3/3kT)\eta = (4\pi a^3/3kT)\eta_0 \exp(\nu\pi r_c^2 c) = \tau_0 \exp(\nu\pi r_c^2 c) \tag{5}$$

where a is the hydrodynamic radius of the diffusing particle. From eq 5 we get

$$\ln \tau = \ln \tau_0 + (\nu\pi r_c^2)c \tag{6}$$

For a real, inhomogeneous gel, the average polymer chain concentration, c_c, can be used instead of c as a first approximation: in fact, after replacing c with c_c, eq 6 becomes virtually identical to the empirical equation (eq 1). However, this approximation does not take into account the partition of the paramagnetic probe among differently dense domains of the swollen gel. If the exchange of the probe molecules between different domains is slow in the ESR time scale, and if the spectral contributions from the different domains are not too different in terms of g values and of hyperfine coupling constants (A), then, according to Windle,[23,29] the overall τ value can be expressed as

$$\tau = \sum p_i \tau_i \tag{7}$$

where p_i is the fraction of the probe molecules present in V_i, and τ_i is the corresponding τ value. The individual values of

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[26] (a) Martini, G.; Burlamacchi, L. *Chem. Phys. Lett.* **1976**, *41*, 129. (b) Martini, G.; Ottaviani, M. F.; Romanelli, M. *J. Colloid Interface Sci.* **1987**, *115*, 87.

[27] *A Treatise on Physical Chemistry*; Taylor, H. S., Glasstone, S., Eds.; Van Nostrand: New York, 1951; Vol. 2.

[28] Nicodemo, L.; Nicolais, L. *Polymer* **1984**, *15*, 589.

[29] Windle, J. J. *Starch/Staerke* **1985**, *37*, 121.

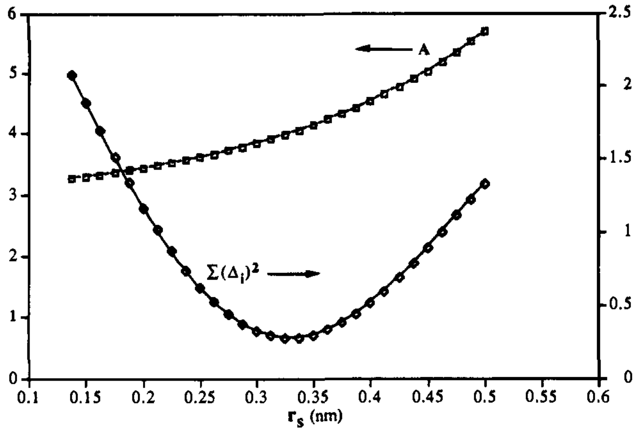

Figure 4. Dependence on r_s of the sum of the squared errors on τ/τ_0 and of the optimized values of A.

p_i can be obtained from the ISEC data and from the distribution coefficients K_i of the probe (eq 10), calculated on the basis of the Ogston model:[22]

$$p_i = K_i V_i / \sum K_i V_i \tag{8}$$

Upon replacing eqs 8 and 5 in eq 7, we obtain for a given matrix

$$\tau/\tau_0 = \sum [K_i V_i \exp(\nu \pi r_c^2 c_i) / \sum K_i V_i] = \sum [K_i V_i A^{c_i} / \sum K_i V_i] \tag{9}$$

$$K_i = \exp[-\pi c_i (r_c + r_s)^2] \tag{10}$$

where $A = \exp(\nu \pi r_c^2)$, and r_s is the molecular radius of TEMPONE.

Volumes of the individual polymer fractions V_i, the corresponding c_i, and the radius of the polymer chain r_c are available from the ISEC characterization. In particular, we chose 0.2 nm as a reasonable value for r_c.[12] Thus, only A and r_s are to be determined. Optimal values of these parameters were calculated by nonlinear regression, in which the sum of squared differences between experimental and computed values of τ/τ_0 was minimized. The dependence of the sum of squared errors on the value of parameter r_s and the relevant optimized values of A, calculated separately for each value of r_s, are shown in Figure 4. This dependence has a well-defined minimum at $r_s = 0.32$ nm. The same value of the molecular radius of TEMPONE was reported by Freed et al.[30] This excellent agreement of the value determined as an adjustable parameter with its assumed physical meaning is a good support to the reliability of the proposed physico-mathematical model. The good agreement between the experimental and the calculated values of τ/τ_0 can be also appreciated in Figure 5.

4. Conclusions

As a general comment, it can be stated that our physicochemical model fits nicely with the observed data and leads to reliable physical conclusions:

(i) The molecular acccessibility of microporous resins to molecules of substantial size can be effectively evaluated by ESR and ISEC techniques, in an integrated way.

(ii) Inside these materials, ESR provides a clear indication on the rotational and (indirectly) translational mobility of probes featured by defined size and lipophilic–hydrophilic character.

(iii) The combined ESR–ISEC approach provides physical evidence for depicting swollen light- and medium-cross-linked resins as concentrated viscous aqueous "solutions" of polymer chains, inside which thermodynamics and kinetics (as well as spectroscopy and photochemistry) of dissolved molecules can be envisaged.

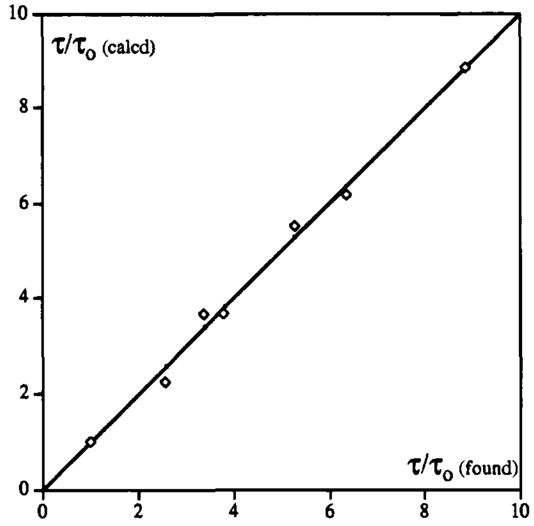

Figure 5. Graphical comparison between experimental and calculated values of τ/τ_0.

(iv) Relatively simple ESR measurements appear to be a promising tool for characterizing microporous supports to be used as reagents, as solid catalysts, or as designable supports in supported metal catalysis.

(v) Conscientious utilization of ESR can relieve those applied researchers who are engaged in polymer-supported bio- or metal catalysis from a great deal of "trial and error"-based experimental efforts.

5. Experimental Section

ISEC Measurements. Full details on sample preparation and chromatographic runs are given elsewhere.[31,32] Deuterium oxide, ribose, xylose, saccharose, raffinose, and polydextranes, which proved to be suitable standard solutes for water as the stationary phase,[26,33] were employed in the investigation described here. Data processing is described in ref 10.

ESR Measurements. Each spectrum was obtained as the sum of 10 scans recorded with an X-band Bruker apparatus at 9.4 GHz (modulation 100 kHz). The temperature was varied stepwise (10–20 °C steps), and every spectrum was recorded twice, both while decreasing and while increasing temperature, in order to verify reproducibility. The rotational correlation times were calculated according to the formula;[34]

$$\tau = (6.5 \times 10^{-10})[(A_0/A_{-1})^{1/2} + (A_0/A_{+1})^{1/2} - 2]\Delta H_{pp}$$

the parameters A_{+1}, A_0, A_{-1} (the intensities of the low-, middle- and high-field lines, respectively) and ΔH_{pp} (peak–peak width of the central line) were obtained directly from the double-derivative spectrum by peak-picking. Preparation of the sample was as follows: millimiter-sized, irregularly shaped lumps of the polymeric material to be analyzed were swollen with a 10^{-4} M aqueous solution of TEMPONE, and the system was allowed to reach equilibrium. Then a few swollen particles were recovered, gently and quickly rubbed with filter paper for removal of external liquid phase, and finally transferred into the ESR tube.

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(30) Hwang, J. S.; Mason, R. P.; Hwang, L. P.; Freed, J. H. *J. Phys. Chem.* **1975**, *79*, 489.

(31) Corain, B.; Corvaja, C.; Lora, S.; Palma, G.; Zecca, M. *Adv. Mater.* **1993**, *5*, 367.

(32) Jeřábek, K.; Setínek, K. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1387.

(33) Crispin, T.; Halász, I. *J. Chromatogr.* **1982**, *239*, 351.

(34) Buchachenko, A. L.; Kovarskii, A. L.; Vasserman, A. M. In *Advances in Polymer Science;* Rogovin, Z. A., Ed.; Wiley: New York, 1974; p 26.