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(35) The effect of A and B polymers having different D_c's (i.e., $D_{c,A} \neq D_{c,B}$) on the diffusion is also clarified from the theory by de Gennes[36] for polymer blends. In this case D_c in eq 37 should be replaced by an effective diffusion constant $D_{c,app}$, $D_{c,app} = D_{c,A}D_{c,B}[1 - 2\chi Z\phi_A\phi_B]/[D_{c,A}\phi_A + D_{c,B}\phi_B]$.
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Cholesteric Liquid Crystalline Phases Based on (Acetoxypropyl)cellulose

So-Lan Tseng, Agostino Valente, and Derek G. Gray*

Pulp and Paper Research Institute of Canada and Department of Chemistry,
McGill University, Montreal, Quebec H3A 2A7, Canada. *Received November 13, 1980*

ABSTRACT: (Acetoxypropyl)cellulose ($\bar{M}_w = 140000$) was prepared by acetylation of (hydroxypropyl)cellulose. The polymer formed a thermotropic cholesteric phase which reflected visible light in the 85–125 °C temperature range. Solutions of (acetoxypropyl)cellulose in acetone containing more than 50 wt % polymer formed a liquid crystalline mesophase. The mesophase birefringence, reflectance, and optical rotatory dispersion were measured as a function of polymer concentration; the results confirmed the cholesteric nature of the mesophase.

Introduction

The (hydroxypropyl)cellulose–water system[1–7] forms the first reported liquid crystalline mesophase based on cellulose. (Hydroxypropyl)cellulose (HPC) also forms mesophases in organic solvents,[5,8] and there is evidence that a broad range of other cellulose derivatives[9–11] and cellulose itself[12] form anisotropic solutions at high concentrations in appropriate solvents. Interest has centered on the production of high-modulus fibers from anisotropic solutions,[9,12] but the cholesteric properties[1,3,10] of these materials may also prove useful. Numerous polymers containing cholesteryl derivatives have been synthesized,[13] but we are unaware of any reports that these display the unique optical properties associated with the cholesteric liquid crystalline state.[14] We feel that the chiral and relatively stiff molecular structure of cellulose, nature's most abundant polymer, may provide an ideal substrate for preparing novel cholesteric materials. This paper describes a new[15] cellulose derivative, (acetoxypropyl)cellulose (APC) (Figure 1), which readily forms cholesteric liquid crystalline solutions with organic solvents; the pitch of the helicoidal structure in these solutions may be varied over a wide range by changing the polymer concentration. The polymer also forms a thermotropic cholesteric phase.

Experimental Section

Preparation of Polymer. (Acetoxypropyl)cellulose was readily prepared by the acetylation of (hydroxypropyl)cellulose. (Hydroxypropyl)cellulose (Aldrich, nominal MW = 100000) (100 g) was dissolved in 300 mL of pyridine, and 370 mL of acetic anhydride was added to the solution. After stirring overnight, the solution was refluxed briefly, allowed to cool, and poured into

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* To whom correspondence should be addressed at McGill University.

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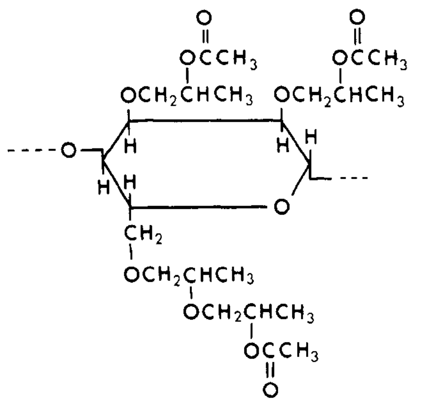

Figure 1. Idealized representation of an anhydroglucose unit of (acetoxypropyl)cellulose with four hydroxypropyl groups and three acetate groups as substituents.

a large excess (~4 L) of water. The APC separated as a white sticky mass with a pearly sheen. After being washed with water to remove reactants and solvent, the polymer was purified by repeated solution in acetone and reprecipitation in water. Alternatively, the use of pyridine may be avoided by simply adding the HPC (100 g) to acetic anhydride (330 g) to give a viscous solution on standing. Acetic acid (30 g) was added to initiate esterification, and the mixture was allowed to stand for 1 week, with brief periods of heating and stirring. The polymer was isolated and purified as above. Final yield after drying was 107 g (~80%) of a cloudy gray tacky material. Properties of the polymers prepared by both methods were very similar; numerical results in the paper refer to the latter sample unless otherwise indicated. On standing in water, the amphiphilic but water-insoluble polymer formed a pearly white soft putty which did not adhere to glass and which was easier to handle than the very sticky water-free polymer.

Infrared spectra of the polymer showed strong peaks at 1735 and 1240 cm^{-1}, as expected for the acetate substituents; a significant peak at 3500 cm^{-1} due to hydroxyl groups indicated that acetylation was not complete. The acetyl content of the polymer was measured by saponifying the APC with a known amount of aqueous sodium hydroxide and then back-titrating the excess base. The acetyl content was found to be 22.7% by weight. Assuming that the molar substitution of the original HPC was 4,[16] the number of acetyl groups per residue was 2.7.

The weight-average molar mass, $\bar{M}_w$, of the sample was measured in acetone solution with a Chromatix KMX6 low-angle laser light scattering photometer. The solutions were filtered with a 0.2-μm Millipore Type FG filter and then passed through the light scattering cell at a flow rate of 0.05 mL/min. Measurements of the Rayleigh factor for each solution were made at a scattering angle of 6–7°. The value for the specific refractive index increment, dn/dc, for APC in acetone, determined with a Brice-Phoenix differential refractometer was 0.100, giving a value for $\bar{M}_w$ of 1.42×10^5, with a second virial coefficient of 1.7×10^{-4} mL mol g^{-2}.

The density of the APC sample was measured with a Weld-type pycnometer; the average of three determinations with n-decane or mesitylene as inert liquid was 1.15 ± 0.02 g/mL. Solution weight fractions were converted to volume fractions with this value for the density of APC and 0.785 g/mL for the density of acetone, on the assumption that mixing involved no volume change. The densities of a series of solutions in acetone were measured with a Paar DMA-02C precision density meter, from which the apparent specific volume of APC in dilute acetone solution was calculated to be 0.825 ± 0.005 mL/g.

Concentrated-Solution Properties. Several series of solutions containing from 10 to 90% by weight APC in acetone and in acetic acid were prepared by weighing appropriate quantities of polymer and solvent into 5-mL glass sample vials and allowing the contents to mix for several weeks. The mixing process was facilitated by periodically inverting the vials. Dilute solutions were clear viscous liquids; on increasing the polymer concentration a faint white precipitate and then a cloudy lower layer became evident. At higher concentrations, the solutions were completely cloudy, showing first rainbow-like iridescence and then reflecting colors which progressed from red through the spectrum to violet at 90 wt % polymer. No sample was used until it appeared visually uniform.

Quantitative handling of these viscous sticky solutions containing relatively small amounts of volatile solvents required care and patience. Concentrations were checked by making replicate weighings of small aliquots using a Cahn Model G electrobalance, carefully evaporating off the solvent, and reweighing to constant weight.

The refractive indices of the concentrated APC solutions were measured with an Abbé refractometer (Carl Zeiss). Dilute isotropic solutions when spread on the prism surfaces gave the usual sharp single line in the viewing telescope, corresponding to the sample refractive index. Samples of the liquid crystalline solutions gave two distinct lines. Following the method used by Schael[17] to measure the birefringence of polymer films, the lines were attributed to the refractive indices in the plane of the prism surfaces and normal to this plane. Thus the difference gives the birefringence of the samples in these directions. Measurements were made in triplicate, about 2 min after spreading the solution on the prism.

Many samples formed cholesteric structures with reflectance bands in the visible region. The wavelength of the reflection band peak was most readily determined by measuring the absorption of light transmitted normal to the sample. A sample of the mesophase was placed between a microscope slide and cover glass with a 75-μm Mylar spacer, and absorption spectra were measured with a Pye-Unicam SP8-150 spectrophotometer. The shape of the spectra changed with time. The freshly prepared sample slide gave a broad diffuse peak; on standing, the peak became sharper, the peak absorption increased, and the peak maximum wavelength, $\lambda_{\max}$, moved to longer wavelengths. After about an hour, $\lambda_{\max}$ reached the constant value which was recorded; after 3–4 h, evaporation of the solvent caused $\lambda_{\max}$ to start to move to shorter wavelengths. The optical rotation of several samples was measured as a function of wavelength with a Jasco Model ORD/UV-5 spectropolarimeter; thinner samples were necessary in order to keep the maximum optical rotation within the range of the instrument. The thickness of the cover glasses and sample layer was measured with a precision micrometer. The ORD spectra changed with time in a manner consistent with the absorption spectra (see Figure 4). Thin-walled 0.5-mm-o.d. quartz capillaries were filled with mesophase by gentle suction, and the scattering of Ni-filtered Cu Kα radiation from a Philips PW1730 X-ray generator was recorded photographically with a Warhus flat-film camera. Optical observations were made with a Reichert polarizing microscope and a Mettler FP52 hot stage.

Errors in measurements resulted primarily from the difficulty of preparing, transferring, and maintaining uniform solutions of known concentration.

Results and Discussion

The (acetoxypropyl)cellulose was isolated as a gray, tacky material, soluble in many polar organic solvents. When a thin layer was placed between a microscope slide and cover glass (either by melting a portion of APC, by solvent casting a film from solution, or by squeezing flat a piece of white, water-swollen APC and drying), the material appeared birefringent. When heated on a hot stage, the layer appeared distinctly purple at ~85 °C; the color changed to longer wavelength at higher temperatures, becoming red at ~125 °C. The birefringence disappeared at 164 °C, and the polymer formed a viscous isotropic melt. This behavior of the solvent-free polymer strongly suggests that APC behaves as a *thermotropic* cholesteric liquid crystal below 164 °C. As a working hypothesis, we may suppose that the cellulose backbone provides sufficient stiffness so that near-parallel arrangements of the chains are favored,[18] the chirality of the anhydroglucose units results in small asymmetric forces between chain segments,

Table I
Refractive Index and Measured Birefringence of (Acetoxypropyl)cellulose in Acetone Solution

vol fraction of APC in soln	refractive index		birefringence × 10^3
0	1.3580		0
0.147^a	1.3805		0
0.229^a	1.3883		0
0.319^a	1.3988		0
0.338^a	1.4032		0
0.366^a	1.4060		0
0.396^a	1.4096	1.4082	1.4
0.416^a	1.4154	1.4130	1.4
0.468^a	1.4233	1.4204	2.9
0.522^a	1.4285	1.4256	2.9
0.579^a	1.4303	1.4271	3.2
0.636	1.4383	1.4337	4.6
0.638^a	1.4333	1.4300	3.3
0.659	1.4406	1.4362	4.4
0.684	1.4428	1.4382	4.6
0.709	1.4452	1.4404	4.8
0.732	1.4472	1.4425	4.7
0.756	1.4493	1.4448	4.5
0.781	1.4515	1.4472	4.3
0.794	1.4528	1.4483	4.5
0.805	1.4538	1.4493	4.5
0.829	1.4565	1.4515	5.0
0.860	1.4585	1.4538	4.7
1.000^a	1.4717	1.4672	4.5

[a] APC sample prepared by acetylation in pyridine.

either directly or via a helical chain configuration,[19] producing the macroscopic helicoidal structure characteristic of the cholesteric state, and the high density of flexible side chains inhibits crystallization and allows the molecules sufficient mobility to achieve their preferred orientation. (A similar picture has been invoked to explain the formation of cholesteric liquid crystalline solutions of HPC.[5]) Recently it has been observed[20] that some HPC samples also form a thermotropic liquid crystalline phase at temperatures above 160 °C.

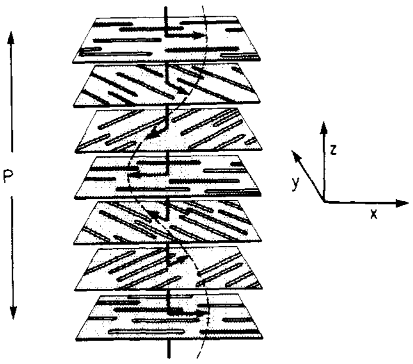

Figure 2. Schematic representation of a planar cholesteric structure of pitch P.

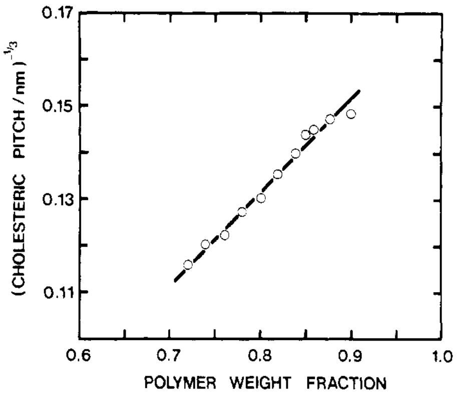

Figure 3. Relationship between the cholesteric pitch of APC–acetone liquid crystalline solutions and the polymer weight fraction.

(Acetoxypropyl)cellulose also forms liquid crystalline solutions with many organic solvents. Here we report on concentrated-solution behavior in acetone. A series of concentrated solutions was prepared, as described in the Experimental Section. After standing for 3 months, the samples were visually examined. The first appearance of a cloudy lower phase requires an APC concentration of ~50 wt % polymer. The clear upper phase is still apparent at 60 wt % but is no longer detectable at 65 wt % polymer. Between 65 and ~80 wt % the samples displayed the faint shimmering colors characteristic of Bragg scattering of visible light; above 80 wt % the samples reflected uniform iridescent colors which ranged from red at the lower concentrations to violet at 90 wt % polymer. Some minor variation in appearance occurred with time and with APC sample. (The sample prepared in pyridine solution showed phase separation and cholesteric colors at slightly lower polymer concentrations.) The liquid crystalline nature of the cloudy phase was readily confirmed by observing the birefringence of the fluid with a polarizing microscope. Measurements of the refractive indices of the solutions with an Abbé refractometer (Table I) clearly indicate the appearance of the birefringent liquid crystalline phase at 40 vol % (50 wt %) polymer. The measurements also give the apparent birefringence of the solution, which in the two-phase region is a mixture of isotropic and liquid crystalline phases. In the two-phase region, the apparent birefringence should increase with the proportion of liquid crystalline phase, as is observed. In the liquid crystalline region, the birefringence appears to be almost constant with concentration from about 60 up to 100 vol % APC, with a value of 0.0046 ± 0.0004. The point at which the birefringence reaches a constant value presumably indicates the transition from two-phase region to pure anisotropic phase, a phase boundary which is difficult to ascertain. Although Table I contains insufficient data to locate the point precisely, the method should be capable of further refinement. The Abbé refractometer thus provides a novel and convenient way to estimate the approximate birefringence of liquid crystalline materials.

de Vries[21] developed a theory to account for the optical properties of planar cholesterics, based on a model of a large number of birefringent layers, each arranged with optic axes slightly displaced from those of neighboring layers in a helicoidal structure, as sketched in Figure 2. According to de Vries, the wavelength, λ_0, of light reflected normally from a planar cholesteric sample is given by

$$\lambda_0 = \bar{\mu} P \tag{1}$$

where $\bar{\mu}$ is the average refractive index of the liquid crystalline phase and P is the pitch of the helicoidal arrangement. The optical rotatory power of the cholesteric structure at wavelengths larger and smaller than that of the reflected light is given by[21]

$$\theta = -\frac{\pi \Delta\mu_c^2 P}{4\lambda^2[1 - (\lambda/\lambda_0)^2]} \tag{2}$$

where θ is the optical rotation in rad/nm of light of wavelength λ nm normal to the samples and $\Delta\mu_c$ is the layer birefringence.

The variation in pitch with APC concentration for a series of liquid crystalline solutions in acetone is illustrated in Figure 3. The pitches were calculated from eq 1, where λ_0 is taken as the wavelength of the maximum of the

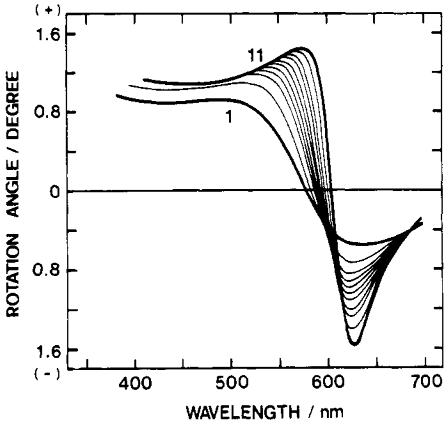

Figure 4. Optical rotatory dispersion of a planar cholesteric layer of (acetoxypropyl)cellulose in acetone: curve 1, 5 min after slide preparation; curve 11, 140 min after slide preparation; intermediate curves, 6-10-min intervals. The sample thickness was 47 μm.

spectrophotometric reflection peak for a thin layer of the solution and $\bar{\mu}$ is taken as the arithmetic mean of the two refractive indices for the appropriate solution concentration. The pitch was found to vary inversely as the third power of the polymer concentration over the accessible concentration range. When plotted as in Figure 3, data points for the 11 solutions gave a straight line (correlation coefficient 0.999) which may be extrapolated to the pure polymer axis at P = 194 nm. A similar dependence on concentration has been observed for HPC in water.[6,22] (The linear dependence prematurely quoted by Werbowyj and Gray[3] is now known to be incorrect.) In contrast, Robinson[23] found that periodic spacing, and hence the pitch, varied inversely as the second power of the concentration for the long-pitch cholesteric structures observed with poly(γ-benzyl L-glutamate) in dioxane. However, Uematsu and Uematsu[24] found that the power dependence of pitch with concentration for several similar polypeptide liquid crystalline solutions depended on the temperature. The significance of these apparent power dependences remains open to question.

The intensity of the cholesteric reflection may be quantified by measuring the optical rotation per unit sample thickness as a function of wavelength. The resultant optical rotatory dispersion curves for APC in acetone resemble those observed for conventional cholesterics[21] and for HPC in water.[1,3] An example is shown in Figure 4. The initial curve was made within 5 min of preparing the slide and shows a reversal of optical activity over a rather broad wavelength range. On allowing the slide to stand, the range becomes sharper, and the wavelength of zero optical activity, λ_0, moves to longer wavelengths. Our explanation is that initially the cholesteric domains in the sample are oriented at random, resulting in a range of reflections whose wavelengths are shifted toward the blue because of the angular dependence of cholesteric reflection.[14] In time, the glass surfaces cause the domains to orient in the planar texture, with the helicoidal axis normal to the glass surfaces. Little change in curve shape is detectable after ~2 h. The final curve shape (curve 11 of Figure 4) is compared with the predictions of eq 2 by plotting θ vs. $(1/\lambda^2)[1 - (\lambda/\lambda_0)^2]$, where θ is measured at wavelengths λ outside the reflection band (i.e., for λ outside the range $\lambda = \lambda_0 \pm {\sim}40$ nm). The slope of the plot is $\pi P \Delta\mu^2/4$, and since P is known from eq 1, the value of the cholesteric layer birefringence, $\Delta\mu_c$, may be measured. Values for three samples are listed in Table II; the values are approximate (±40%) because of errors in measuring sample thickness, deviations from eq 2 due to nonattainment of perfect planar orientation, and neglect of the wavelength dependence of $\bar{\mu}$ and $\Delta\mu_c$.[25]

Table II
Cholesteric Layer Birefringence Values for Three (Acetoxypropyl)cellulose-Acetone Solutions

λ_0	606	451	418
P/nm	419	311	290
sample thickness/μm	47	39	35
birefringence $\Delta\mu_c$	0.0028	0.0025	0.0033

Despite these uncertainties, it is evident that the value of $\Delta\mu_c$ calculated from the optical rotation of the liquid crystalline phase using the de Vries theory (Table II) and the values for the layer birefringence $\Delta\mu$ measured with the Abbé refractometer (Table I) are of the same order of magnitude. More precise measurements of both birefringence values are required, but the data confirm semiquantitatively that the APC-acetone system forms a true cholesteric liquid crystalline phase.

X-ray diffraction of the APC-acetone mesophase gives a diffuse ring with a d spacing of 1.54 nm at 73 wt % (65 vol %) polymer and d = 1.35 nm at 87 wt % (82 vol %) polymer. The corresponding values for P, interpolated from Figure 3, are 645 nm at 73 wt % and 323 nm at 87 wt %. If the d spacings are taken to be the average distance between adjacent polymer chains, then the apparent average angle between adjacent molecules, measured normal to the helicoidal axis, is approximately $360d/P$ degrees, or 0.86° at 73 wt % and 1.5° at 87 wt %. Preliminary measurements indicate that d varies inversely with the amount of polymer in solution; as shown above, P varies as the inverse third power of the polymer weight fraction, and so the average angle between adjacent chains should vary inversely as the square of the average distance of separation for liquid crystalline solutions containing 70-90 wt % APC in acetone. Examination of this and other chiral polymer mesophases over a wider concentration range is required to relate polymer concentration and molecular structure to the striking macroscopic optical properties of these materials.

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Osmotic Deswelling of Gels by Polymer Solutions

J. Bastide,[†,§] S. Candau,[‡] and L. Leibler*[,†]

Centre de Recherches sur les Macromolécules, 67083 Strasbourg Cedex, France, Laboratoire d'Acoustique Moléculaire, ERA au CNRS, Université Louis Pasteur, 67070 Strasbourg Cedex, France, and Faculté des Sciences, Ile de Saulcy, 57000 Metz, France.
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ABSTRACT: Thermodynamic properties of swelling equilibria of polymer networks immersed in solutions of linear polymers are studied. Measurements of the swelling degree of a series of styrene gels in semidilute solutions of high-molecular-weight polystyrene in benzene have been performed. A considerable deswelling with respect to gels swollen in a pure solvent is observed. Within the experimental accuracy no chains permeated into the gel phase. A new scaling approach is developed to describe the swelling of gels in polymer solutions. This method permits calculation of both the swelling degree and partition coefficient (proportion of free linear chains permeating into the gel). Good agreement with experimental data for both semidilute and dilute regimes is found. Some new quantitative predictions are made concerning the swelling by lower molecular weight semidilute solutions. Measurements of elastic moduli of osmotically deswollen gels and their dependence on gel monomer concentrations are reported.

I. Introduction

Polymer networks swollen in a good-quality diluent deswell when transferred to a solution of a high-molecular-weight linear polymer in the same solvent.[1-5] The extent of deswelling depends essentially on the osmotic pressure of the solution in which the gel is immersed. It was long ago proposed to use this property to measure the solvent–polymer interaction parameter or the linear polymer molecular weight.[3,4] Studies hitherto reported have mainly dealt with the case of gels in dilute polymer solutions. The aim of the present work is to study the thermodynamic properties of gels in the presence of more concentrated (semidilute) polymer solutions.

We have performed deswelling experiments on a series of polystyrene networks of different structure immersed in polystyrene–benzene solutions of concentration ranging from 5% to 30%. A spectacular deswelling degree (1.5–6 times) has been observed. This offers new possibilities of studying the equilibrium properties of gels under strong isotropic compression. In particular, important information about local conformation and dynamics of chains in the compressed state of the gel may be obtained by inelastic light scattering and by small-angle neutron scattering from deswollen gels.[6]

The theoretical discussion presented in this paper gives a phenomenological, thermodynamic interpretation of the experimental results we have obtained. The essential difficulty encountered in theoretical studies of swelling of gels is to find an appropriate form of the free energy and in particular to relate its elastic part to some microscopic parameters characterizing the network (e.g., the radius of gyration of network chains).[7-12] The scaling approach proposed here does not require the detailed knowledge of the variation of these microscopic parameters during the swelling (deswelling) process. It permits us to calculate the deswelling degree and the proportion of linear chains permeating into the gel phase (the partition coefficient). The results are compared with available experimental data for both the semidilute regime (reported in this work) and dilute solutions.[5] Good agreement is found.

To get additional information about the scaling form of the elastic energy, we have also performed stress–strain measurements and determined the elastic moduli of swollen gels. The results are presented in the next section, in which the deswelling experiments are also described.

Table I

Anionic Gels

sample	mol wt of precursor	[DVB]/[LE]	C_p PS concn prior to cross-linking	swelling degree in pure benzene
54	34 000	5	0.091	20.5
64	12 500	3	0.109	9.8
65	12 500	3	0.146	8.5

Radicalar Gels

sample	concn of St prior to cross-linking	concn of DVB prior to cross-linking	swelling degree in pure benzene
B7	0.3	0.010	16
B12	0.3	0.013	8.5

II. Experimental Section

Samples and Techniques. In Table I are listed the principal characteristics of the polystyrene networks and their swelling equilibrium in benzene. Samples 54, 64, and 65 were prepared by a synthesis previously described, using anionic block copolymerization of styrene and divinylbenzene (DVB).[13] In the first step, bifunctional living polystyrene is prepared at low

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[†] Centre de Recherches sur les Macromolécules.
[‡] Université Louis Pasteur.
[§] Faculté des Sciences, Ile de Saulcy.

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