scatterings. The coefficients are mutually dependent through the function $\alpha(\mathbf{r},t)$ and its Fourier transform. Note that eq 9 is a direct generalization of eq 6 to a system in which the dependence of diffusion on concentration is not specified.

Experimental Considerations

In many experiments, $I(\mathbf{q},0)$ is much greater than $I(\mathbf{q},\infty)$, and therefore the difference between eq 1 and 2 is not large. Under such circumstances, it becomes difficult to determine from an experiment whether eq 1 or eq 2 provides a better fit, and in many cases, reasonable diffusion constants can be obtained by setting $I(\mathbf{q},\infty) = 0$.

Ideal experiments for comparison with the equations are the investigations of Bartels et al.[4,5] of diffusion in hydrogenated polybutadiene (HPB). In these studies, thick (several micrometers) alternate layers of HPB and its deuteriated homologue (DPB) were prepared, and diffusion was brought about by heating for various lengths of time. In any measurable q range, $I(\mathbf{q},0)$ was equal to zero, and scattering intensities increased with time. The growth of scattering intensity was entirely independent of q and dependent on the initial thickness of layers of the polymer. See Figure 1 of ref 4 and Figure 5 of ref 5. Incidentally, the equations of Bartels et al. are identical with eq 1 if $I(\mathbf{q},0)$ is set equal to zero.

A recent investigation of polystyrene (PSH) and polydeuteriostyrene (PSD) by small-angle neutron scattering was carried out by Anderson and Jou.[6] In their experiment, $I(\mathbf{q},0)$ is much greater than $I(\mathbf{q},\infty)$ at low q. However, in the range of $\mathbf{q}$ where reasonable estimates were possible, the growth of the equilibrium scattering curve showed no dependence on q. This is consistent with Bartels et al.[4,5]

In an experimental arrangement similar to that used by Bartels et al., Stamm[7] has presented small-angle neutron scattering measurements of diffusion from alternating layers of PSH and PSD. His measurements show a growth of scattering intensity which is also independent of q.

Conclusions

1. The original equations of Summerfield and Ullman[1] for determination of diffusion constants by small-angle scattering have been generalized. The generalized result includes the original results and the Cook equation as limiting cases.

2. Measurements of diffusion of polymer in the melt by small-angle neutron scattering by different groups all yield scattering growth terms which are independent of q, consistent with the previous work of Summerfield and Ullman.[1]

Acknowledgment. Professor A. Z. Akcasu called the authors' attention to the contradiction between the Cook–Binder and Summerfield–Ullman equations. His comments and criticisms provided valuable guidelines for this work. Support of the National Science Foundation under Grant DMR8217460 is gratefully acknowledged.

Registry No. PSH, 9003-53-6; neutron, 12586-31-1.

References and Notes

(1) Summerfield, G. C.; Ullman, R. *Macromolecules* **1987**, *20*, 401.
(2) Cook, H. *Acta Metall.* **1970**, *18*, 297.
(3) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(4) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2707.
(5) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(6) Anderson, J. E.; Jou, J. H. *Macromolecules* **1987**, *20*, 1544.
(7) Stamm, M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) 1987, *28*, 2, 56.

Communications to the Editor

A Novel Route to Polypyrazoles

Introduction. Polymers composed of heterocyclic repeat units in the backbone have proven to be among the most thermally stable materials produced to date.[1] A particularly interesting subclass of heterocyclic polymers are polypyrazoles. Among the routes available to these materials, a commonly used approach is cycloaddition. The addition of bis-nitrilimines[2a], bis-sydnones[2b] and bis-azides[2c] to diacetylenes have all successfully produced polypyrazoles. Recently, Bass[3] and coworkers have used the addition of bis-hydrazines to acetylenic ketones and esters to prepare thermally stable polypyrazoles.

We have been studying the polymerization of relatively easily prepared bis-chlorovinylidene cyanides with diamines to give exceptionally stable polyenaminonitriles.[4] We were interested to see if we could prepare the analogous enhydrazinonitriles and subsequently cyclize them to pyrazoles (Scheme I).

Experimental Section. All solvents were purified and dried by standard laboratory procedures.

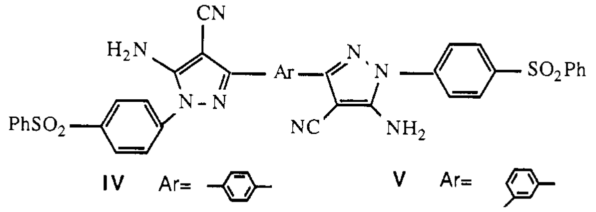
Instrumentation. Infrared (IR) and Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Model 298 spectrophotometer and a Perkin-Elmer Model 1800 Fourier transform infrared spectrometer, respectively. NMR spectra were recorded on a Varian Model XL-200 spectrometer operating at 200 MHz for ^{1}H and 50.3 MHz for ^{13}C spectra. Some ^{13}C NMR were also obtained on an IBM Model WP/SY 100 spectrometer operating at 25.1 MHz. Chemical shifts are recorded in parts per million from hexamethyldisiloxane, used as an internal standard, when DMSO-d_6 was the solvent. Viscosities of polymer solutions were measured by using Cannon-Ubbelohde viscometers. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a Perkin-Elmer System 7 instrument interfaced with a Perkin-Elmer Model 7500 computer. Heating rates were 10 or 20 °C/min for DSC and 10 °C/min for TGA. Elemental analyses were performed by Galbraith Laboratories, Inc., P.O. Box 51610 Knoxville, TN 37950-1610, and Robertson Laboratory, Inc., 29 Samson Ave., P.O. Box 761, Madison, NJ 07940. The presence of thermally stable structural moieties in the compounds under discussion leads to carbonaceous residues causing low carbon values to be obtained in some instances.

Monomer Syntheses. 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene and 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene,[4] 4-hydrazinophenyl ether dihydrochloride,[3] and (4-hydrazinophenyl)sulfone[5] were prepared by previously reported procedures.

Model Compound Syntheses. 3,3′-(1,4-Phenylene)bis[1-(4-(phenylsulfonyl)phenyl)-4-cyano-5-amino-

0024-9297/88/2221-2644$01.50/0

pyrazole] (IV). To a solution of [4-(hydrazinophenyl)phenyl]sulfone[6] (1.6566 g, 6.68 mmol) and triethylamine (0.6800 g, 6.7 mmol) in dry *N*-methyl-2-pyrrolidone (NMP) (10 mL), cooled to 0 °C, was added, with stirring under a nitrogen atmosphere, a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (1.0007 g, 3.34 mmol) in dry NMP (10 mL). The reaction mixture turned brown and then (2–3 min) light yellow. The mixture was stirred under nitrogen and gradually warmed to room temperature (60–70 min) and reaction was continued for 2 h. The yellow solid which formed was filtered, washed repeatedly with hot methanol, and dried in vacuo to yield the desired bispyrazole (1.7100 g, 70%): mp >400 °C dec; FTIR (KBr) 3400–3200, 2220, 1635, 1595, 1560, 1515, 1320–1295 (m), 1160, 1110, 985, 845, 695 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.10 (s, 4 H), 7.60–7.68 (m, 6 H), 7.83 (d, *J* = 9 Hz, 4 H), 7.91 (s, 4 H), 7.95–7.99 (dd, *J* = 8.1, 1.7 Hz, 4 H), 8.08 (d, *J* = 9 Hz, 4 H); ^{13}C NMR (DMSO-d_6) δ 71.92 (*C*CN), 114.95 (C*C*N), 124.64, 126.34, 127.36, 128.65, 129.75, 131.44, 133.82, 139.57, 140.72, 150.30 (Ar C), 141.32 (*C*C$_6$H$_4$), 152.32 (*C*NH$_2$). Anal. Calcd for $C_{38}H_{26}N_8O_4S_2$: C, 63.14; H, 3.62; N, 15.50. Found: C, 62.88; H, 3.64; N, 15.45.



IV V

Model compound V was also synthesized as described above in 64.3% yield from 1,3-bis(1-chloro-2,2-cyanovinyl)benzene and [4-(hydrazinophenyl)phenyl]sulfone:[6] mp >400 °C dec; FTIR (KBr) 3450–3000, 2220, 1635, 1595, 1560, 1520, 1500, 1450, 1410, 1320, 1310, 1160, 1105, 845, 750, 720, 685 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.08 (s, 4 H), 7.31–7.68 (m, 7 H), 7.81 (d, *J* = 8.7 Hz, 4 H), 8.28 (m, 1 H); ^{13}C NMR (DMSO-d_6) δ 70.26 (*C*CN), 112.96 (C*C*N), 121.83, 122.78, 124.99, 125.51, 126.99, 127.52, 129.47, 131.92, 137.76, 138.90, 148.73 (Ar C), 139.48 (*C*C$_6$H$_4$), 151.57 (*C*NH$_2$). Anal. Calcd for $C_{38}H_{26}N_8O_4S_2$: C, 63.14; H, 3.62; N, 15.50. Found: C, 62.08; H, 3.98; N, 15.24.

Polymer Synthesis. All three polymers were synthesized by using the following typical procedure.

Poly[(4-cyano-5-amino-3,1-pyrazolediyl)-1,4-phenylene-(4-cyano-5-amino-1,3-pyrazolediyl)-1,4-phenylene] (I). A dry 100-mL, three-necked, round-bottomed flask was fitted with a mechanical stirrer, an addition funnel with a nitrogen inlet, and reflux condenser connected to a mineral oil bubbler. The assembly was charged with (4-hydrazinophenyl)sulfone (1.8595 g, 6.68 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.7500 g, 6.68 mmol), and dry *N*-methyl-2-pyrrolidone (20 mL). To this solution, stirred under nitrogen and cooled to 0 °C, was added, dropwise, a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (2.00 g, 6.68 mmol) in dry NMP (13.6 mL). The color of the reaction mixture changed to dark brown and then to light yellow (ca. 2 min). The solution was stirred under nitrogen at 0 °C for 1 h, heated at 70 °C for 24 h, cooled to room temperature, and poured into vigorously stirred water. The precipitated polymer was filtered, dissolved in *N*,*N*-dimethylformamide (DMF), precipitated in methanol, and dried at 100 °C in vacuo for 48 h to yield light yellow polymer I in 86% yield: FTIR (film) 3420–3200, 2220, 1635, 1595, 1555, 1520, 1430, 1410, 1320, 1300, 1160, 1105, 985, 850, 760, 600 cm^{-1}; ^{1}H NMR (DMSO-d_8) δ 7.11 (s, 4 H), 7.83–7.91 (m, 4 H), 8.13 (d, *J* = 8.5 Hz, 4 H); ^{13}C NMR (DMSO-d_6) δ 71.95 (*C*CN), 114.93 (C*C*N), 124.772, 126.37, 129.00, 131.43, 139.26, 150.34 (Ar C), 141.56 (*C*C$_6$H$_4$), 153.30 (*C*NH$_2$).

Spectral Data for Polymer II (Yield, 98.5%): FTIR (film) 3400–3200, 2220, 1670, 1635, 1595, 1560, 1520, 1500, 1410, 1325, 1298, 1160, 982, 850, 800, 760, 640 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.10 (s, 4 H), 7.59 (t, *J* = 7.6 Hz 1 H), 7.83–7.93 (m, 4 H), 8.13 (d, *J* = 8.5 Hz, 2 H), 8.31 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 70.21 (*C*CN), 112.89 (C*C*N), 121.79, 122.86, 125.07, 127.13, 127.53 (Ar protonated C), 129.41, 137.41, 148.71 (Ar quat C), 139.58 (*C*C$_6$H$_4$), 151.54 (*C*NH$_2$).

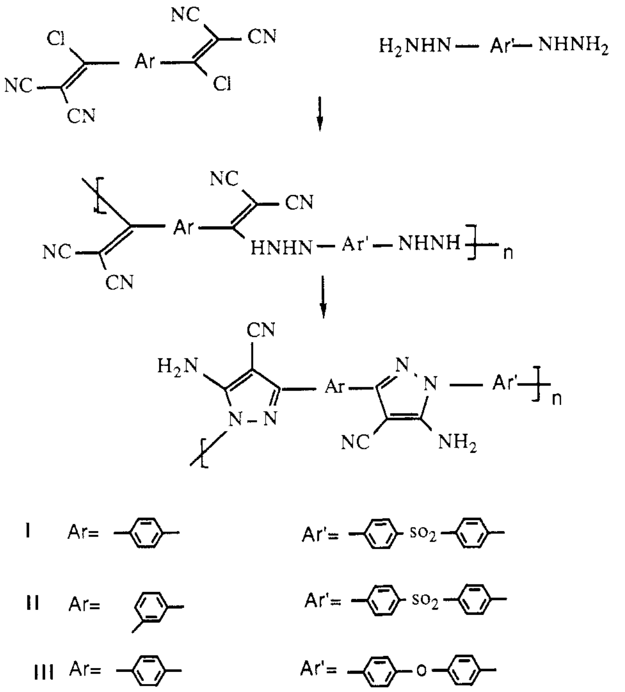
Spectral Data for Polymer III (Yield, 84.2%): FTIR (film) 3400–3200 (m), 2220, 1670, 1630, 1560, 1520, 1500, 1240, 1165, 840, 620 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.83 (s, 4 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.9 Hz, 2 H), 7.92 (s, 4 H); ^{13}C NMR (DMSO-d_6) δ 69.25 (*C*CN), 113.44 (C*C*N), 117.65, 124.68, 124.91 (Ar protonated C), 129.78, 130.96, 151.27 (Ar quat C), 147.50 (*C*C$_6$H$_4$), 154.15 (*C*NH$_2$).

Atomic Oxygen and Oxygen Plasma Resistance. Atomic oxygen was generated by passing high-purity oxygen (Linde) through an all-glass, low-pressure discharge tube approximately 1 m long, having aluminum electrodes. O$_2$ entered the tube approximately halfway between the electrodes and high power (400 W) was applied to form atomic oxygen at a concentration of 15–20% by volume. Atomic oxygen thus formed in the discharge was carried in a molecular oxygen stream through a glass connecting tube to an all-glass (45 mm o.d.) plug-flow reactor where the oxygen atoms reacted with a polymer film. Oxygen plasma resistance studies were made by using a Technics Planar Etch II apparatus (200 W, 140 mTorr).

Results And Discussions. Synthesis. A useful analogy[7] between a dicyanomethylidene group (=C(CN)$_2$) and a carbonyl group indicates that the two units have similar inductive and resonance effects, and many well-known reactions of carbonyl groups have been shown to have parallels, in terms of chemical reactivity, with dicyanomethylidene groups. More importantly, the presence of a dicyanovinylidene moiety ensured that the initial product of the vinylic nucleophilic substitution reaction could cyclize to a stable heteroaromatic unit. The vinylic nucleophilic substitution reaction is known to proceed rapidly and few side reactions occur.[4] When bishydrazines were reacted with bischlorovinylidene cyanides, the intermediate enhydrazines were never isolated but continued reacting to give high molecular weight, thermally stable, and oxygen-resistant polypyrazoles. The structure of the polypyrazoles could be either 1,3- or 1,5-disubstituted. Spectroscopic comparison with authentic small molecules of either possible structure revealed that only 1,3-entrainment could be detected in the polymers as prepared here. Inherent viscosities of polymers I and III were 1.62 dL/g (concentration, 0.31 g/dL) and 1.70 dL/g (concentration, 0.42 g/dL), respectively, when measured in concentrated sulfuric acid at 25 °C. Polymer II had an intrinsic viscosity of 0.35 dL/g in *N*,*N*-dimethylacetamide at 25 °C. All the polymers were soluble in polar aprotic solvents like DMF, NMP, DMAc, and DMSO. Fingernail-creasable films could be cast from solutions in these solvents. The ^{1}H NMR, ^{13}C NMR, and IR of the polymers corresponded well with those obtained for model compounds IV and V (Scheme I).

Thermal Stability. In the most practical sense, thermal stability means the ability of a material to maintain the requried mechanical properties such as strength, toughness, or elasticity at a given high temperature coupled with resistance to thermooxidative degradation.[1] Requirements for a polymer to be thermally stable are, then, high melting or softening temperature and the presence

Scheme I



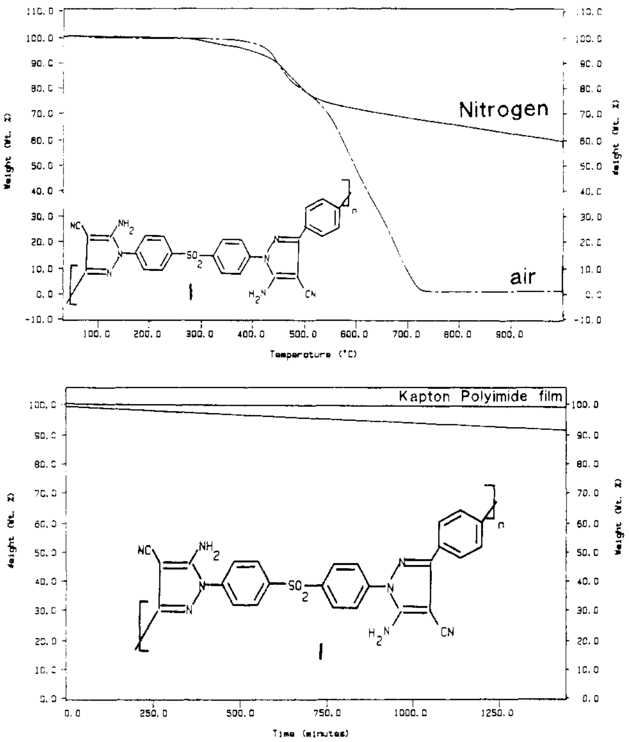


Figure 1. (a, top) TGA of polymer I in air and nitrogen atmosphere. (b, bottom) Isothermal aging of polymer I and Kapton in air at 300 °C.

of chemical bonds of high dissociation energy. While fulfilling these requirements and hence possessing good thermal stability, most such polymers suffer from the disadvantages of very high transition temperatures and/or poor solubility. This combination makes processing very difficult. Pyrazole units in the polymer backbone, along with flexible ether and sulfone linkages, have allowed us to synthesize polymers having thermal stability comparable to Kapton and good processability.

Table I
Thermogravimetric Analysis

polym	50% wt loss temp, °C (air)	residual wt %, 1000 °C (N_2)
I	600	60
II	505	54
III	500	60

[a] Isothermal aging for 24 h.

Table II
Atomic Oxygen and Oxygen Plasma Resistance

polym	% wt loss at. oxygen[a]	% wt loss oxygen plasma[b]
I	6.0	16.6
II	4.5	11.9
III	100.0	52.5

[a] 3.5 h. [b] 64 min.

Table III
^{13}C NMR Data Indicating Charge Asymmetry

comp	δ(CCN), ppm	δ(CNH_2), ppm	comp	δ(CCN), ppm	δ(CNH_2), ppm
I	71.95	153.30	IV	71.92	152.32
II	70.21	151.54	V	70.26	151.57
III	69.25	154.15			

As shown in Figure 1a for polypyrazole I, as a typical example, the polymer retains almost 60% of its mass at 1000 °C in nitrogen and at 575 °C in air. Comparison with Kapton, under isothermal aging conditions (300 °C in air for 24 h, Figure 1b), indicates that more than 90% of its mass is retained. The results in Table I similarly indicate excellent thermal stability of polymers II and III. In a separate experiment it was found that the films of these polymers retained almost the same degree of flexibility even after heating at 200 °C in vacuum. The calorimograms of these polymers did not show any glass transition temperatures. Optical microscopy, in the case of polymer I, indicated a broad glass transition (100–300 °C) and some degree of crystallinity after heating. For polymers I and III, it was found that they became almost insoluble in the aprotic solvents from which the films were cast, after heating at 200 °C. Presumably, further reaction between amine and cyano groups leads to cross-linking.

Atomic Oxygen and Oxygen Plasma Resistance. Results obtained from exposure to both atomic oxygen and oxygen plasma indicated the following order of stability: II > I ≫ III (Table II). The presence of electron-donating ether oxygen atoms makes polymer III more susceptible to oxidative degradation. Efforts are under way to make polypyrazoles, with varying degree of electron richness, to gain further insight into this structure property relationship.

^{13}C NMR Data. The ^{13}C NMR data of model compounds and polymer indicate strong polarization of a double bond bearing conjugated amino and nitrile groups in a pyrazole moiety ($NCC{=}CNH_2$) (Table III).

A poly(enaminonitrile), synthesized earlier in our laboratory, showed similar bond polarization and its dielectric constant was found to be as high as 8.[8] These initial observations have prompted us to conduct experiments to study dielectric behavior and second harmonic generation (SHG) response of these polymers, which will be reported at a future date.

Conclusions. We have successfully employed electrophilic divinylbenzene monomers as synthetic equivalents of diacid chlorides to prepare high molecular weight, oxidation-resistant polypyrazoles containing charge asymmetry. These materials hold promise for applications as components of ablative coatings and composite materials and possibly advanced applications in the areas of polymeric dielectric materials and polymers having nonlinear optical properties.

Acknowledgment. Prof. Robert Reeves, Matt Rutten, and S. Y. Kim were instrumental in obtaining oxidation resistance data. Prof. R. G. Bass generously provided information on the preparation of the hydrazines. Their contribution is gratefully acknowledged. This work has been supported, in part, by a grant from the Office of Naval Research.

Registry No. I (copolymer), 115077-22-0; I (SRU), 115077-25-3; II (copolymer), 115077-23-1; II (SRU), 115077-26-4; III (copolymer), 115077-24-2; III (SRU), 115077-27-5; IV, 115077-20-8; V, 115077-21-9; O_2, 7782-44-7; [4-(hydrazinophenyl)phenyl]sulfone, 70714-83-9; 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene, 103134-51-6; 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene, 108090-23-9.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.

(2) (a) Stille, J. K.; Harris, F. W. *J. Polym. Sci. Polym. Chem. Ed.* **1968**, *6*, 2317. (b) Stille, J. K.; Bedford, M. A. *Ibid.* **1968**, *6*, 2331. (c) Gilliams, Y.; Smets, G. *Makromol. Chem.* **1969**, *128*, 263.

(3) Connell, J. W.; Bass, R. G.; Sinsky, M. S.; Waldbauer, R. O.; Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2531.

(4) Moore, J. A.; Robello, D. R. *Macromolecules* **1986**, *19*, 2667.

(5) Tokunga, D.; Hattori, T.; Kubo, T. *Chem. Abstr.* **1957**, *52*, 112911.

(6) This monofunctional hydrazine was prepared from hydrazine hydrate and (4-chlorophenylphenyl)sulfone (Aldrich Chemical Co.) by the method employed for the synthesis of bifunctional monomer as described in ref 5.

(7) (a) Wallenfels, K. *Chemia* **1966**, *20*, 303. (b) Wallenfels, K.; Thiem, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 261.

(8) (a) Moore, J. A.; Robello, D. R., submitted for publication in *Macromolecules*. (b) Robello, D. R. Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1986.

J. A. Moore* and Parag G. Mehta
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

Received March 21, 1988

Large-Scale Heterogeneities in Randomly Cross-Linked Networks

Large-scale imperfections in network structures are known[1,2] to influence the solvent permeability, the diffusion of small and large molecules (electrophoresis), and more indirectly the swelling and the elastic properties of gels. Light-[3-5] and neutron-scattering[6] studies have shown the existence of concentration heterogeneities at submicrometer scales in gels synthesized under very different conditions. The competition between dilution effects and an effective attraction induced by chemical cross-linking often produces density fluctuations already in the reaction bath (all kinds of syneresis).[1,7] Here we would like to focus on a more paradoxical situation when the large-scale concentration heterogeneities do not appear during the gelation but only in the gel swollen at equilibrium. We discuss a random cross-linking of semidilute solutions of long precursor chains and argue that self-similar cross-linking density fluctuations may exist even far beyond the gel point and are revealed by the swelling of the network.

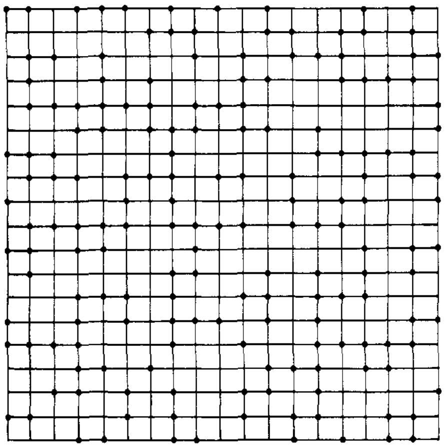


Figure 1. Schematic representation of a two-dimensional reaction bath well above the chain gelation threshold. The size of the lattice site is ξ_r. For sake of simplicity, the chains, which are random walks on this lattice, are not shown on the figure. Black dots represent the interchain cross-links, placed at random.

Consider a reaction bath well in the semidilute regime. It can be visualized as a melt of "blobs" of size ξ_r, which scales as the screening length of the excluded volume interaction or as the distance between interchain contact points. Introduce now, at random and rapidly, some cross-links in this solution. Depending on the concentration in the reaction bath φ_r, a fraction of them will react on the same chain and will form small loops:[8] these junctions are lost with respect to the interchain gelation process. Only the tie points that form interchain bridges will contribute to the elasticity. Let us call $\rho(\varphi_r)$ the interchain cross-linking density, i.e., the ratio of the number of interchain tie points and monomer units. We avoid here the delicate question of estimating the number of intrachain cross-links and use $\rho(\varphi_r)$ instead of the total number of introduced cross-links. We can thus consider that everything happens as if a certain fraction of permanent cross-links was placed at random upon the interchain contact points, which can be viewed as forming the sites of a lattice of coordination number 4 (and unknown topology). This means that the problem can also be regarded as a site percolation,[9] on a lattice with a site having the blob size (cf. ref 10). As pointed out first by Daoud,[10] the statistical cross-linking of a semidilute solution contains therefore two separate questions: the "true" gelation of the chains and the "percolation" of the blobs. We would like to focus here on a frequent regime of chain length, concentration (φ_r), and cross-linking density when the two following conditions are satisfied:

(i) $\rho(\varphi_r) \gg 1/Z$, where Z denotes the weight-average polymerization index of the precursor chains.

(ii) $P_b = g\rho(\varphi_r) \lesssim P_c$, with P_b denoting the fraction of linked blobs and g being equal to the number of monomer units per blob. P_c is the gelation threshold in the percolation model.

The first condition ensures that a sufficiently regular gel is formed: one expects a vanishing sol fraction and even a small fraction of dangling ends (with respect to the number of elastically effective strands). On the other hand, condition ii implies that a noticeable disorder remains in the spatial repartition of cross-links: a given junction may or may not be neighbor to another one on the lattice of the interchain contact points, as illustrated schematically in Figure 1. When junctions are located on neighboring lattice sites, a "frozen blob" is formed. When swelling, it will be difficult to move these cross-links apart from each other since they are connected by a chain segment which is already in a optimal excluded volume conformation. Frozen blobs are often connected and form clusters of first topological neighbors.[11,12] The important point is that the