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Elastic Modulus and Degree of Cross-Linking of Poly(ethyl acrylate) Networks

B. Erman,[†] **W. Wagner,**[‡] **and P. J. Flory***

Department of Chemistry, Stanford University, Stanford, California 94305.

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ABSTRACT: Poly(ethyl acrylate) of high molecular weight has been cross-linked quantitatively by 1,12-diaminododecane at concentrations ranging from ca. 1.0×10^{-5} to 12×10^{-5} mol cm^{-3}. The amidation was carried out by heating at 110–120 °C for 72 h in the presence of a small proportion of *p*-toluenesulfonic acid. Equilibrium tensions f were determined for swollen and unswollen samples at elongations α ranging from ca. 1.05 to the point of rupture ($\alpha \approx 3.0$–1.4, depending on the degree of cross-linking). Reduced forces $[f^*] = (f/A^0)(V^0/V)^{1/3}(\alpha - \alpha^{-2})^{-1}$, where A^0 and V^0 are the unswollen cross section and volume, respectively, and V is the swollen volume, were extrapolated to α^{-1}, those for swollen samples being nearly independent of α. Reduced forces in this limit for unswollen samples approximate those for swollen samples, which are in good agreement with values calculated according to theory for phantom networks. The permanent (topological) entanglements that must inevitably occur in abundance in random networks evidently do not affect the stress significantly. Critical examination of published results for other polymer networks supports the same conclusion, i.e., that the contribution of topological entanglements to the reduced force is generally small or negligible.

Introduction

The force f in a uniaxially stressed rubber network can be expressed according to theory[1,2] as the sum of two terms as follows:

$$f = f_{\mathrm{ph}} + f_{\mathrm{c}} \tag{1}$$

The first of the terms, f_{ph}, represents the contribution of the corresponding phantom network; the other, f_{c}, is due to the space-filling requirements of real chains as opposed to their phantom analogues.[1,2] A phantom network is defined[3] as the hypothetical one consisting of chains having the configuration-statistical characteristics of the real chains but without their material properties. The phantom chains do not exclude one another spatially, and they may transect each other freely. They are constrained only by the (permanent) connections of their ends to network junctions, e.g., to cross-linkages.

The theory of phantom networks[3,4] yields a uniaxial stress–strain relationship of the familiar form

$$f_{\mathrm{ph}} = (\xi kT/L^0)(V/V^0)^{1/3}(\alpha - \alpha^{-2}) \tag{2}$$

where ξ is the cycle rank of the network,[3] or the number of independent circuits therein, L^0 is the rest length, V^0 is the volume of the network in its reference state,[5] and $\alpha \equiv L/L_i$ is the extension ratio for the deformed specimen of length L relative to its rest length L_i (i.e., in the state of isotropy) at the prevailing volume V. If V^0 may be identified with the volume of the unswollen network, then V/V^0 equals the swelling ratio. For a perfect network consisting of ν chains joined by junctions of functionality φ

$$\xi = \nu(1 - 2/\varphi) \tag{3}$$

Substitution of this relation in eq 2 reduces the latter to the result inferred by Graessley[6] and Duiser and Staverman[7] from treatments of micronetworks comprising several junctions.

Let the reduced force, or reduced nominal stress, be defined by

$$[f^*] \equiv f/A^0(V/V^0)^{1/3}(\alpha - \alpha^{-2}) \tag{4}$$

where A^0 is the cross-sectional area of the specimen in its state of reference. Then,[1,2] according to eq 1–4

$$[f^*] = (\xi kT/V^0)(1 + f_{\mathrm{c}}/f_{\mathrm{ph}}) \tag{5}$$

or, for a perfect network of functionality φ

$$[f^*] = (\nu kT/V^0)(1 - 2/\varphi)(1 + f_{\mathrm{c}}/f_{\mathrm{ph}}) \tag{6}$$

The universally observed departures of the relationship of stress to strain from predictions of phantom network theory find explanation in the dependence of the ratio $f_{\mathrm{c}}/f_{\mathrm{ph}}$ on strain.[1,8–10] The contribution f_{c} to the force is attributable to the exclusion of the real chain from the space occupied by other chains. This restriction greatly reduces the number of configurations accessible to the network. The associated reduction of the configurational partition function is not, in itself, of consequence, but its dependence on strain is. That the effect of exclusion of overlaps must decrease with dilution is obvious. Further considerations lead to the conclusion that the effect should diminish, relative to the total stress, with extension also.[1,11] Inasmuch as the junctions and their pendent connections are most vulnerable to the restrictions imposed by the effects of mutual exclusion, the theory[1,2] considers the fluctuations of junctions about their mean positions to be restricted on this account in a manner that depends on the strain.

The general features of the relationship of stress to strain are well reproduced by theory developed on this basis.[8–10] Measured stresses for axial deformations of poly(dimethylsiloxane) networks covering a fourfold range of extension and a sixfold range of compression on the same sample are well represented by the theory.[10] Arbitrary assignment of a single parameter governing the magnitude of f_{c} as a function of strain suffices.

At high extensions and at high degrees of swelling the ratio $f_{\mathrm{c}}/f_{\mathrm{ph}}$ vanishes.[1,2] Hence, by extrapolating the observed reduced force to high extensions (in the manner suggested by the Mooney–Rivlin empirical relation) or, preferably, by conducting measurements on swollen samples, one may obtain the limiting value of the reduced force, i.e., the reduced force for the phantom network given by

$$[f^*]_{\mathrm{ph}} = \xi kT/V^0 \tag{7}$$

The effective value of the network connectivity ξ may thus be deduced from elasticity experiments. This value of ξ may be compared with the degree of interlinking deduced from a quantitative characterization of the structure of the network.

[†] School of Engineering, Boğaziçi University, P. K. 2 Bebek, Istanbul, Turkey.

[‡] Paganiniweg 8, D-8236 Burghausen, Federal Republic of Germany.

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Table I
Summary of Experimental Results on PEA Networks

diamine, equiv % of COOR	catalyst, equiv % of NH_2	free amine by titration, %	extent of reaction[a] p	$[f^*]_{ph}$(calcd),[b] N mm^{-2}	linear swelling ratio[c]	$[f^*]_0$(exptl), N mm^{-2}	
						swollen	unswollen
0.25	4.0	6.0	0.90	0.027	2.06	0.018	0.018[d]
0.36	3.5	1.5	0.95	0.044	2.00	0.027	0.050
0.85	1.9_4	0.0	0.98	0.110	1.81	0.112	0.120
1.59	1.9	0.0	0.98	0.207	1.66	0.210	0.200
2.50	2.0	0.3	0.98	0.325	1.44	0.280	0.260

[a] Calculated from titration of free amine plus amine retained by catalyst. [b] Calculated from chemical constitution according to eq 7. [c] Determined on unstressed samples in bis(2-ethoxyethyl) ether. [d] Result obtained (±0.03) from measurements at 80 °C, not included in Figure 1.

Before proceeding with this comparison, it is important to observe that the foregoing procedure makes allowance for one of the characteristics that distinguishes the real network from its phantom counterpart but not the other. It takes account (approximately) of the configurational restrictions due to the finite volume occupied by the real chain but ignores the integrity of the chains that precludes their transection of one another. The profusion of permanent entanglements embedded inextricably in the topology of the network as a consequence of this manifest property of a real chain remains to be considered. These entanglements are often assumed to act like additional junctions and thus to enhance the effective connectivity, or degree of interlinking, embodied in ξ. In view of the permanence of these entanglements, their postulated enhancement of ξ is taken to be independent of strain. Hence, the form of the stress–strain relationship, including the effect of swelling, should be unaffected.

The copious interpenetration of chains in a typical network implies a very high degree of entanglement. The number of topological entanglements incident to a given chain may be on the order of 50 or greater.[1,3,9] An entanglement clearly cannot be equivalent to a cross-linkage in its effect on the stress. While it is conceivable that the summated effects of all the entanglements might enhance the elastic response of the real network to a measurable degree, it does not necessarily follow that this must be so. The issue is one to be referred to experiments.

Numerous investigations have been carried out for the purpose of assessing the extent to which the effective degree of interlinking deduced from measurements of stress departs from the "chemical" value of ξ. Quantitative determination of this latter value usually is difficult. A substantial body of evidence from investigations in which the network structure has been reliably characterized, and in which the elasticity measurements permit reliable estimation of the limiting value of the reduced force, indicates that the thus corrected stress may approximate the value calculated for a phantom network. The contribution of entanglements to the stress appears to be small. Results have been summarized by Mark[12] and also by one of the present authors.[9]

In the present investigation we have devised methods for quantitatively cross-linking atactic poly(ethyl acrylate) (PEA) by use of a diamine. The reaction is one of the utmost simplicity and therefore less susceptible to the uncertainties attending more complicated processes applied to other polymers. The cross-linked polymer is readily amenable to the elasticity measurements required to determine the reduced force in the limit of high degrees of swelling and of strain.

Experimental Section

Preparation and Structural Characterization of Samples. The linear PEA polymer (atactic) from which the networks were prepared was a commercial product from Rohm and Haas Co. Its viscosity-average molecular weight was 3×10^6. The polymer was dissolved in acetone and precipitated with water several times in order to remove stabilizers and other additives. Acetone and water were removed from the finally precipitated polymer by heating at 60 °C under vacuum for 6 days.

Cross-linking was effected by 1,12-diaminododecane which had been purified by recrystallization. The amidation reaction was catalyzed by *p*-toluenesulfonic acid. Weighed quantities of polymer, diamine, and catalyst were dissolved in methylene chloride. Amounts of diamine were chosen in the range 0.25–2.5 equiv % of amine relative to ester groups. The catalyst amounted to 2–3 equiv % of the amine. The solution, containing ca. 4% polymer by weight, was poured into a Teflon mold and the solvent was allowed to evaporate at room temperature over a period of 5 days. The PEA film thus obtained was placed in a gas-tight aluminum reaction vessel equipped with O-ring seals, Teflon fittings, and gas inlet and outlet tubes. The vessel was flushed with dry argon from which oxygen had been removed by passage through chromium(II) perchlorate, then over KOH pellets, and finally over Drierite. The gas outlet led to a trap cooled with dry ice for removal of ethanol released in the reaction and then to an exit bubble valve filled with silicone oil. All tubing was of Teflon. After 3 h of flushing with argon, the vessel and contents were heated to 110–120 °C for 72 h. A slow stream of argon adjusted to a rate of ca. 2 bubbles/min was maintained throughout the period of heating. After the reaction vessel had cooled, it was rinsed with acetone. Nonaqueous potentiometric titration[13,14] of the contents of the trap and the acetone used to rinse the vessel was carried out in order to determine diamine that had escaped from the sample. The titrant was 0.1 N perchloric acid in glacial acetic acid.[15] The amount of diamine thus determined was less than 1% of the total in all cases.

Unreacted amine in the PEA network also was determined by potentiometric titration. Thin films of the cross-linked polymer (0.1–0.2 g, ca. 0.1 mm in thickness) were swollen 24 h in dioxane prior to titration. The surrounding dioxane solution was stirred gently to facilitate equilibration during titration. After each addition of acid, diffusion into the film was allowed to proceed for 1–2 h. Addition of lithium chloride to the solution facilitated equilibration. Titers were measured to $\pm 2 \times 10^{-4}$ mL.

In a series of pilot experiments, samples were removed and titrated after 6, 24, 48, and 72 h at 110 °C. The free amine decreased from 65% at 6 h to <3% at 72 h. Titrations performed on samples used in the elasticity measurements, which were heated 72 h at 110–120 °C, yielded the results given in the third column of Table I.

A parallel set of experiments was carried out with laurylamine at a level of 2 equiv %. The samples were soluble in dioxane and could be titrated readily. After 72 h at 120 °C, the titer of free amine was nil, in accord with the titrations of the insoluble networks obtained with the diamine. There was no indication of degradation in the course of the reaction with laurylamine, from which we infer that the primary chain length of the PEA was little affected during the cross-linking process.

The networks of the five samples used in this investigation are characterized by the data in the first four columns of Table I. The degree of cross-linking was calculated from the extent of reaction p determined from titration of the network, with allowance for the amine groups retained by the catalyst. On the assumption that amidation of the two amine groups of the diamine

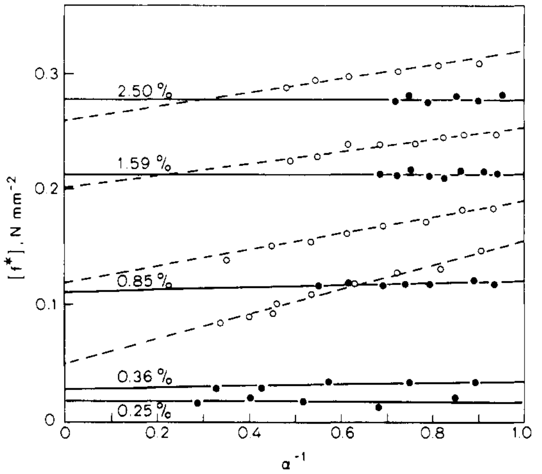

Figure 1. Reduced forces $[f^*]$ plotted against the reciprocal of the elongation α for the samples identified by the equivalent percentages of diamine; see Table I. Filled and open circles represent results on swollen and unswollen samples, respectively.

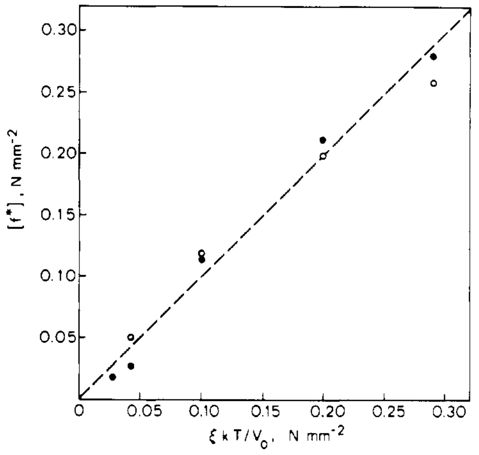

Figure 2. Limiting values of reduced forces $[f^*]_0$ for swollen (filled circles) and unswollen (open circles) samples plotted against chemically determined values of $[f^*]_{ph}$, the reduced force for a phantom network. The diagonal dashed line denotes equivalence of elastically effective cross-linkages to their number ξ determined chemically.

proceeds independently, the number of moles of cross-linkages equals the product of p^2 and the number of moles of diamine. The cycle rank ξ equals the degree of cross-linking in the case of tetrafunctional junctions, provided that the primary molecules are indefinitely long. For molecules of finite length, the correction that takes account of imperfections due to free ends of chains is $(1 - 2M_c/M)$, where M is the number-average molecular weight of the primary molecules and M_c is the average molecular weight of a chain between cross-linked units. In the sample E-1 of lowest degree of cross-linking, $2M_c/M < 0.1$. Hence the factor above may be replaced by unity with negligible error and eq 7 may be employed to calculate $[f^*]_{ph}$ with ξ therein identified with the number of cross-linkages. Values of this quantity calculated from the stoichiometric ratio of diamine to ester groups, the degree of reaction, and the density of PEA, 1.095 g cm^{-3} at 25 °C,[16] are given in the fifth column of Table I.

Uniaxial Tension Measurements. Tension measurements in elongation were performed on strips of cross-linked PEA having dimensions of 0.5 × 3 × 30 mm. Samples were swollen by immersion in bis(2-ethoxyethyl) ether for 24 h to allow equilibration. They were then removed from the diluent. Experiments were conducted in air at room temperature (ca. 25 °C), the diluent being sufficiently nonvolatile to render evaporation negligible in the course of the measurements. Before performance of the experiment, the swollen sample was subjected to several loading and unloading cycles. The relationship of tension to elongation was then determined by applying successively increasing loads to the lower end of the suspended specimen and measuring the vertical distance between fiducial marks after equilibrium was reached at each load. Small dye spots placed ca. 1 cm apart on the unstrained, unswollen sample served as the marks. Their distance apart was measured with a cathetometer accurate to 0.01 mm. Although the lengths of the swollen specimens became constant after 5 min, 15 min was allowed at each stage before recording the final reading. The time required for unswollen samples to reach equilibrium varied from a few minutes for the sample with the higher degrees of cross-linking to about 12 h for those lightly cross-linked.

Results

In Figure 1 the reduced forces $[f^*]$ calculated according to eq 4 are plotted against α^{-1} for the several samples. Filled circles represent results of tension measurements on swollen samples and open circles denote results on unswollen samples. Intercepts of the straight lines determined by the method of least squares are listed in the last two columns of Table I. Whereas the slopes for the swollen samples are small or negligible, those for the unswollen samples are appreciable, in keeping with observations on other polymers. The intercepts for swollen and unswollen samples agree within limits of experimental error for the three samples of highest degrees of cross-linking. The difference between the intercepts for the sample cross-linked with 0.36 equiv % of diamine may be due to the difficulty of reaching equilibrium with this unswollen sample.

The intercepts $[f^*]_0$ at the limits $\alpha^{-1} = 0$ for swollen and unswollen samples are plotted in Figure 2 against the chemically determined value of $[f^*]_{ph}$ given in the fifth column of Table I. Extrapolation is inconsequential for the swollen samples. Intercepts thus obtained obviously are more accurate than those for unswollen samples. Both sets of points in Figure 2 are in good agreement with the dashed line of unit slope. Correspondence of the limiting value $[f^*]_0$ with $[f^*]_{ph}$ for a phantom network is thus demonstrated.

Discussion

The "plateau modulus" observed for linear PEA by dynamic mechanical measurements[19] would translate to a contribution of 0.16 N mm^{-2} to $[f^*]$ on the assumption that entanglements invoked to account for this plateau are "trapped" upon forming the network and consequently contribute to the elastic modulus of the network.[17,18] Three of the five samples of PEA exhibit reduced forces falling below this value. The experimental results presented in Figure 2 extrapolated to the origin within experimental error; they would not admit of an intercept that is greater than ca. 10% of the plateau modulus.

Reduced forces for the unswollen networks at small strains exceed the values calculated for phantom networks from the chemically determined connectivity ξ. The departures are within the range of predictions of recent theory,[1,2] i.e., $f_c/f_{ph} < 2$ at $\alpha = 1$, for three of the samples when unswollen. For the fourth (0.36%), it is much larger, according to the results presented. The enhancements of $[f^*]$ for the various samples at $\alpha = 1$ virtually vanish upon swelling and therefore cannot be ascribed to permanent entanglements that augment the effective degree of cross-linking. Coincidence of the observed limiting reduced forces with the calculated values of $[f^*]_{ph}$, within limits of experimental error, demonstrates that effects of topological entanglements are negligible in polyacrylate networks. The hypothesis that entanglements latent in the polymer prior to cross-linking contribute appreciably to the elastic response of these networks clearly is untenable.

Turning to other systems, we note that poly(dimethylsiloxane) (PDMS) networks have been most extensively investigated with the object of relating the elastic modulus to network structure. Mark and co-workers[20-23] have exploited the reaction of hydroxyl-terminated linear PDMS chains with either tetraethyl silicate or triethoxyvinylsilane to prepare networks having functionalities φ of 4 and 3, respectively. The reaction is virtually quantitative. They eliminated the factor $1 + f_c/f_{ph}$ in eq 6 by extrapolating reduced forces to $\alpha^{-1} = 0$. For tetrafunctional networks with $\nu kT/V^0$ ranging from 0.1 to 0.6 N mm^{-2}, Llorente and Mark[22] found "structure factor" ratios $[f^*]_0(\nu kT/V^0)^{-1} = 0.8 \pm 0.16$ compared with the theoretical value of 0.50 for a phantom network. For trifunctional networks covering a similar range of degrees of interlinking, Mark and Llorente[23] found 0.54 ± 0.11 for this ratio compared with 0.33 for a phantom network. These results indicate reduced forces in the limit $\alpha^{-1} = 0$ which are somewhat greater than for phantom networks, but the magnitudes of the disparities are marginal compared to experimental errors. The structure factor ratios exhibited no discernible dependence on ν/V^0 over sixfold ranges, from which it was concluded that trapped entanglements do not make a significant contribution.

Valles and Macosko[18] prepared PDMS networks by coupling linear chains terminated by H–Si(CH$_3$)$_2$–O– groups with tri- and tetravinyl compounds in the presence of a platinum complex. Dynamic shear moduli were measured at low frequencies as the reaction progressed, the extent of the reaction being followed by measuring the infrared absorption of residual Si–H.[24] The elastic moduli thus determined at small strains exceeded by factors of 2–5 the values deduced from the extent of interlinking. The disparity, attributed by Valles and Macosko[18] to entanglements, would be narrowed, but not eliminated, by taking account of the factor $1 + f_c/f_{ph}$, which they dismissed.[25]

Recently Falender, Yeh, and Mark[27] and Oppermann and Rehage[28,29] have reported investigations on tetrafunctional PDMS networks prepared by the same chemical procedure used by Valles and Macosko,[18] conditions being so chosen as to ensure virtual completion of the reaction. Falender et al.[27] measured the elastic retractive force over a range of extensions. Extrapolation to $\alpha^{-1} = 0$ yielded $[f^*]_0(\nu kT/V^0)^{-1} = 0.60$. Oppermann and Rehage[28,29] measured elastic moduli of their samples at low frequencies (10^{-1}–1 Hz) in torsion. Moduli thus obtained were confirmed by static measurements at small elongations. They obtained $[f^*](\nu kT/V^0)^{-1} = 0.5$, in apparent agreement with theory, but without correction for the dependence of $[f^*]$ on strain through the factor $1 + f_c/f_{ph}$. Correction therefore presumably would lower the result to ca. 0.35. Confirmatory results were obtained by using PDMS networks prepared by cross-linking unmoidified PDMS with dicumyl peroxide at 150 °C,[28,29] degress of cross-linking being estimated from the kinetics of decomposition of the peroxide. Both Falender et al.[27] and Oppermann and Rehage[28,29] found the structure factor ratios $[f^*](\nu kT/V^0)^{-1}$ to be independent of the degree of cross-linking. As these authors point out,[27-29] this observation is irreconcilable with an appreciable contribution from trapped entanglements.

The results of these investigations[27-29] obviously cast doubt on those of Valles and Macosko[18] on PDMS networks prepared according to the same procedure. They are more nearly in accord with those obtained by end-linking the hydroxyl-terminated siloxanes.[20-23] Whereas Oppermann and Rehage's[28,29] results point to limiting values of $[f^*]_0$ somewhat below those for phantom networks, Mark and co-workers[22,23,27] find values somewhat greater than phantom network theory predicts. The divergence is comparatively small, however.

Allen and co-workers[30] have investigated the elastic moduli of quantitatively cross-linked networks of polystyrene and of poly(propylene oxide). In both systems they found limiting values of ca 0.7 for the ratio $[f^*]_0(\nu kT/V^0)^{-1}$.

Kraus and Moczvgemba[31] investigated a series of end-linked polybutadienes (PBD) with functionalities in the range $\varphi = 4$–6 or more. Their results yield 0.64 ± 0.15 for the structure factor ratio compared with 0.50–0.75 for phantom networks having functionalities in the estimated range. Dossin and Graessley,[17] on the other hand, found much higher values of 1.8–3.5 for this ratio for networks formed from PBD chains (92% 1,4 units). One of us suggested previously[9] that spatially nonuniform cross-linking with high-energy electrons used by Dossin and Graessley to effect network formation may have vitiated their evaluation of the relation of degree of cross-linking to dose. The presence of a very small fraction of crystalline aggregates is a more plausible explanation of the high values for the ratio above. Crystallization is implicated by the extraordinarily protracted relaxation of stress reported by Dossin and Graessley,[17] from 1 to 30 days being required for equilibration. This explanation is supported by the observation[17] that an "excessively long time" was required for equilibration of samples with lower degrees of cross-linking, in which the tendency for furtherance of crystallization upon elongation should have been more pronounced.

In sum, previous experimental results indicate that the reduced force extrapolated to the limit $\alpha^{-1} = 0$ approximates the value calculated for a phantom network having the same chemical constitution, i.e., calculated directly from the cycle rank ξ. Thus, critical assessment of published experimental results does not yield substantial evidence for a major contribution to the stress from topological entanglements.

It is apparent that determination of ξ (or of ν for perfect networks) requires the utmost pains in the control of stoichiometry and in the performance of accurate chemical analyses. Elastic measurements should preferably be conducted on swollen networks for the twofold purpose of enhancing the rate of relaxation and of reducing the magnitude of the term f_c/f_{ph}, thereby circumventing the difficulties of reliably extrapolating to $\alpha^{-1} = 0$.

Note Added in Proof. Since this paper was submitted, measurements have been carried out at 80 °C on unswollen specimens of the two samples of lowest degrees of cross-linking, 0.25 and 0.36 equiv %, respectively. The rate of equilibration proved to be much faster at this temperature, which is ca. 100 °C above the glass transition. Values of $[f^*]$ found for the latter sample (0.36%) are somewhat lower than those presented in Figure 1; at $\alpha = 1$, $[f^*] = 0.13$ N mm^{-2}. For the sample of lowest degree of cross-linking, $[f^*] = 0.055$ N mm^{-2} at $\alpha = 1$. This value is only one-third of the plateau modulus for PEA, the fact notwithstanding that it is dominated by the contribution f_c; compare f_0 given in the last column of Table I.

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References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(2) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363.
(3) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(4) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651. James, H. M.; Guth, E. *Ibid.* **1947**, *15*, 669. *J. Polym. Sci.* **1949**, *4*, 153.
(5) Flory, P. J. *Trans. Faraday Soc.* **1961**, *57*, 829.
(6) Graessley, W. W. *Macromolecules* **1975**, *8*, 186, 865.
(7) Duiser, J. A.; Staverman, A. J. "Physics of Non-crystalline Solids"; Prins, J. A., Ed.; North-Holland Publishing Co.: Amsterdam, 1965; pp 376-87.
(8) Erman, B.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1115.
(9) Flory, P. J. *Polymer* **1979**, *20*, 1317.
(10) Pak, H.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1845.
(11) Ronca, G.; Allerga, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(12) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Chem. Phys.* **1979**, *70*, 5324.
(13) Huber, W. "Titrations in Nonaqueous Solvents"; Academic Press: New York, 1967.
(14) Gyenes, I.; Cohen, D.; Millar, I. T. "Titrations in Nonaqueous Media"; Van Nostrand, New York, 1967.
(15) The assistance of Mr. E. H. Meier in providing us with procedures for performance of the nonaqueous titrations and in making equipment available to us for this purpose is gratefully acknowledged.
(16) *Encycl. Polym. Sci. Technol.* **1964**, *1*, 299.
(17) Dossin, L. M.; Graessley, W. W. *Macromolecules* **1979**, *12*, 123.
(18) Valles, E. M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 673.
(19) Janáček, J.; Hrouz, J. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 53*, 283.
(20) Mark, J. E.; Sullivan, J. L. *J. Chem. Phys.* **1977**, *66*, 1006.
(21) Mark, J. E.; Rahalkar, R. R.; Sullivan, J. L. *J. Chem. Phys.* **1979**, *70*, 1794.
(22) Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1979**, *71*, 682.
(23) Mark, J. E.; Llorente, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 632.
(24) Valles, E. M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 521.
(25) Valles and Macosko's[18] assertion that the reduced force is sensibly independent of strain (i.e., that the Mooney–Rivlin C_2 is negligible) is at variance with the behavior of PDMS networks universally observed by other investigators. In comparing their results with recent theory,[26] they incorrectly infer that displacement of junctions should be fully affine at small strains. In effect, they ascribe values of 3 and 2 to $1 + f_c/f_{ph}$ for functionalities $\varphi = 3$ and 4, respectively. These are upper bounds only. Actual values should fall substantially below these limits, even at small strains.[26]
(26) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(27) Falender, J. R.; Yeh, G. S. Y.; Mark, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7353.
(28) Oppermann, W.; Rehage, G. Preprints, IUPAC Symposium on Macromolecules, Mainz, Sept 1979; p 1360.
(29) Oppermann, W., dissertation submitted to the Technischen Universität Clausthal for the degree of Doctor of Science, June 22, 1979. We are indebted to Professor Rehage and Dr. Oppermann for making this dissertation available to us.
(30) Walsh, D. J.; Allen, G.; Ballard, G. *Polymer* **1974**, *15*, 366. Allen, G.; Holmes, P. A.; Walsh, D. J. *Faraday Discuss. Chem. Soc.* **1974**, *57*, 19. Allen, G.; Egerton, P. L.; Walsh, D. J. *Polymer* **1976**, *17*, 65.
(31) Kraus, G.; Moczvgemba, G. A. *J. Polym. Sci., Part A* **1964**, *2*, 277.

Electric Dipole Moments of DNA in Aqueous Solutions as Studied by the Reversing-Pulse Electric Birefringence

Kiwamu Yamaoka* and Koichiro Matsuda

Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku,
Hiroshima 730, Japan.

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ABSTRACT: Reversing-pulse electric birefringence (RPEB) study shows that the electric field orientation of native calf thymus DNA ($M_r = 4.4 \times 10^6$) and sonicated fragments ($M_r = 1.24 \times 10^5$) is accounted for by induced dipole moments originating from the interaction of the counterions (Na^+ and Mg^{2+}), which redistribute on the DNA surface, with the externally applied field. The moments are induced much faster than the overall molecular rotation of DNA with no extremum in the RPEB signals, except for the high molecular weight Na-DNA, which did not obey the Kerr law. The RPEB behavior of DNA in aqueous solutions is discussed with theoretical calculations.

The current consensus is in support of the notion that electric dipole moments are responsible for the orientation of DNA in aqueous solutions by an externally applied electric field.[1,2] However, the nature of the electric moments of DNA has long been controversial and is unresolved as yet. The orientation of an un-ionized rigid rodlike polymer in an electric field may be ascribed to the torque exerted by the field on its permanent dipole moment (μ) and the polarizability anisotropy ($\Delta\alpha = \alpha_{33} - \alpha_{11}$).[3] By virtue of its nearly palindromic structure, DNA should have only a negligible μ, if any. Nevertheless, there have been numerous reports on the apparent permanent dipole moment of DNA, deduced from measurements of dielectric[4,5] and electrooptical properties.[6-8]

Experimental results have been interpreted with three mechanisms: (1) counterion fluctuation,[9] (2) asymmetric counterion flow,[10] and (3) ionic atmosphere polarization.[11] The last of these seems to explain the orientation behavior of DNA adequately, since the electric birefringence (or dichroism) signal (Δn) of DNA in strong fields fits an orientation function based on the variables μ and $\Delta\alpha$.[12,13] In order to verify the orientation by counterion-induced dipole moments, the transient mobility of the counterion condensed on the DNA surface should be measured.

One of the direct physical methods is reversing-pulse electric birefringence (RPEB), introduced by O'Konski and Pytkowicz[14] and put on a theoretical basis by Tinoco and Yamaoka.[15] Theoretical calculations of RPEB demonstrated that the signal Δn of a DNA solution should, after rapid reversal of a square pulse, show an extremum Δ_m after time t_m if it possesses either a permanent dipole moment (Figure 1 of ref 15) or a slow-induced dipole moment (Figure 4 of ref 15). The signal remains without an extremum if DNA is oriented by either $\Delta\alpha$ or a fast-induced dipole moment. These induced moments may result from the redistribution of counterions along the long axis of the DNA chain with a relaxation time of τ_3. The overall rotational relaxation time of DNA around its short

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