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Elastic Behavior of Hydrophilic Polyurethane Networks Prepared from Poly(dioxolane)

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ABSTRACT: Poly(dioxolane) (PDXL) gels are prepared by an end-linking procedure upon reacting α,ω-dihydroxy-PDXL chains with a polyisocyanate. Mechanical and swelling measurements are carried out on various swollen samples of PDXL networks. The experimental results concerning the moduli (G) can be explained if account is taken of the contribution of trapped entanglements (Langley–Graessley model). Data arising from equilibrium swelling measurements in dioxane and in water are used to calculate the Flory–Huggins interaction parameter χ_{12} of the system: This method of determination is independent of the type of model used to evaluate the elastic free energy. A linear dependence of χ_{12} versus v_2—the polymer volume fraction of the gel—is found. The degradation behavior of these networks in acidic aqueous media is investigated as well.

1. Introduction

Hydrogels—i.e., water-swollen gels—have been extensively studied for the past three decades and are currently used in many diversified applications. Of particular interest are those synthetic hydrogels exhibiting a good compatibility with living tissues: They are used in biomedical devices such as contact lenses, prosthetic materials, membranes for controlled drug release, etc. The hydrophilic character of these materials usually results from the presence of functions such as OH, COOH, NH, or SO_3H (carried by the backbone), but it can be due as well to the nature of the backbone, as in the case of poly(ethylene oxide) networks. As an extension of our earlier studies on hydrogels[1,2] we report in this paper on the synthesis and characterization of a new type of hydrogels involving elastic chains of poly(dioxolane). The repeat units of this polymer contain both oxyethylene and acetal groups, conferring to the chain both hydrophilicity and some instability in acidic medium. It was anticipated that networks able to swell and to keep their shape in neutral and basic media, though easily degradable upon changing the pH to acidic, would be of interest. The need for such materials is particularly acute in biomedical engineering.

Poly(dioxolane) (PDXL) is obtained by cationic polymerization of dioxolane under conditions chosen to favor the so-called activated monomer mechanism.[3a] Under these conditions the polymer formed is to a large extent linear and telechelic, fitted at both chain ends with hydroxy functions. The networks are prepared by an end-linking process upon reacting these α,ω-dihydroxy-PDXL chains with a polyfunctional isocyanate according to methods described in previous reports. The present investigation focuses on the characterization of PDXL networks with regard to their elastic behavior in the swollen state (in dioxane and in water) within the limits of small deformations. The results are compared with the predictions of theories of rubber elasticity. The contribution of topological interactions, such as trapped entanglements, to the equilibrium properties is discussed as well. The swelling data are analyzed within the framework of the Flory–Rehner hypothesis. The interpretation proposed is, however, independent of the models generally used to calculate the elastic free energy.

2. Experimental Section

Network Synthesis. The samples of poly(dioxolane) (PDXL) were prepared according to a procedure that is discussed elsewhere.[3b] Prior to its use, dioxolane (DXL) was purified by distillation over sodium.

The **polymerization of dioxolane** was carried out in the bulk at 50 °C in a dry oxygen-free atmosphere: the polymerization was initiated by triflic acid in solution in methylene chloride in the presence of ethylene glycol (EG). The amount of diol introduced was determined by the M_n selected, as M_n is determined by the [DXL]/[EG] mole ratio. After 3 h, *tert*-butylamine was added in order to neutralize the active sites. The salts were removed by filtration of a carbon tetrachloride solution of the raw polymer. The last protonic traces were eliminated by addition of barium oxide. After a second filtration, the polymer was finally freeze-dried.

Size exclusion chromatography (GPC) was used to characterize the molecular weight distribution of the linear poly-DXL samples. Their molecular weight averages were calculated by using a calibration curve established with well-defined PEO samples. Their content in hydroxy functions—located at the chain ends—was determined by two different methods: (i) ^{19}F NMR of the end groups after reaction with CF_3COCF_3,[4] and (ii) chemical titration by means of (diphenylmethyl)potassium in THF medium. Drops of the latter compound were added until the medium turned slightly red, asserting a quantitative metalation. The values of M_n arising from these two methods (assuming that each molecule carries two OH groups) as well as the values expected and those given by GPC are listed in Table I.

Network Formation. The cross-linking agent—Desmodur N 75 (DN 75)—was provided by Bayer. As it is obtained by reaction of hexamethylene diisocyanate with water, it is a mixture of homologues: The distribution of functionalities as determined by GPC shows the existence of at least eight peaks for this batch. The number-average and the weight-average functionalities were estimated to be $f_n = 6.3$ and $f_w = 10$ (Table II).

The synthesis of PDXL networks was performed according to an end-linking procedure worked out for PEO networks. The α,ω-dihydroxy-PDXL was reacted with DN 75 in anhydrous dioxane at 60 °C using stoichiometric amounts of the reagents. After a fixed reaction time—usually 15 days—the gels were allowed to swell to equilibrium in an excess of dioxane. The soluble fraction was extracted, the solvent being replaced every other day. Water-swollen gels were obtained after a slow solvent exchange procedure.

The equilibrium swelling degrees of all our samples were determined in dioxane and in water, and the elastic moduli were measured. The methods used have been described in a previous paper.[1]

Methods Used. Determination of the Critical Molecular Weight M_c and Characterization of the Plateau Modulus.

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Table I
Comparison of the Expected Number-Average Molecular Weights of Eight PDXL Samples with the Values Obtained from GPC, ^{19}F NMR, and Chemical Titration Using (Diphenylmethyl)potassium

$M_{n,th}$[a]	$M_{n,GPC}$	$M_{n,titr}$[b]	$M_{n,NMR}$[c]
1000	900	1020	980
1500	1520	1500	
2000	1900	1750	1680
2000	1900	1700	1650
4000	3500	2950	3080
6000	5580	4320	
7000	6530	6130	
10000	11200	7980	

[a] From the dioxolane to ethylene glycol mole ratio. [b] By chemical titration using (diphenylmethyl)potassium. [c] By ^{19}F NMR on the adduct with hexafluoroacetone.

Table II
Distribution of Functionalities of the Cross-Linking Agent

mass at peak	wt fraction, %	mol fraction, %	functionality f
170	0.7	4.6	2
460	2.2	5.4	3
680	31.0	51.0	4
1170	20.1	19.2	6
1640	13.0	8.9	10
2180	10.1	5.1	15
3250	9.5	3.3	18
4000	13.4	2.5	20

Table III
Newtonian Viscosity η_0 of Various PDXL Samples in the Domain of Molecular Weights Ranging from 1000 to 10 000

M_n	log M_n	η_0, Pa·s^{-1}	log η_0
1120	3.05	1.61×10^2	2.21
1700	3.23	2.31×10^2	2.36
2780	3.45	8.67×10^2	2.94
3300	3.52	1.46×10^3	3.16
5170	3.71	2.50×10^4	4.40
9400	3.96	3.67×10^4	4.56
10200	4.01	4.38×10^4	4.64
11400	4.06	1.20×10^5	5.08

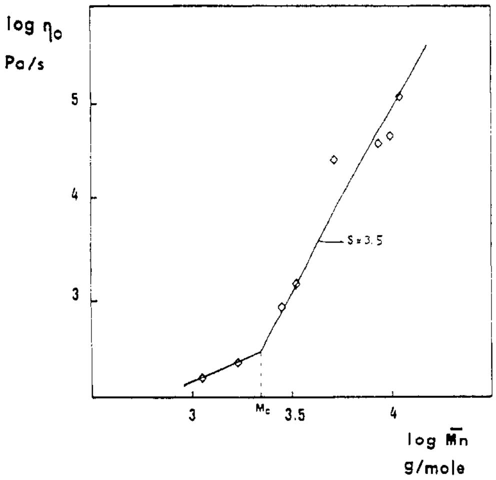

Figure 1. log η_0 plotted against log M_n for eight samples. The line has slope 3.4 on the right and 1.0 on the left.

Eight of our linear PDXL samples were submitted to dynamic oscillatory shear deformation. The measurements were carried out in the bulk at 60 °C. The frequency sweep extends from 0.1 to 100 rad/s. From G' and G'' measured as a function of ω, the dynamic viscosity η^* is calculated and plotted vs ω. As ω tends toward 0, η^* tends to the Newtonian viscosity η_0, the value of which is listed in Table III. The plot of log η_0 as a function of log M_n evidences the onset of entanglements (Figure 1): Below M_c, η_0 is proportional to M_n (slope = 1), and beyond M_c, η_0 is found to increase with the 3.5 power of molecular weight, in agreement with Bueche's predictions.[5] In the case of PDXL M_c is close to 2200.

The plateau modulus $G°_N$ of the PDXL—which characterizes the entanglement network—is determined from measurements of G' and G''. The plateau zone—where both G' and G'' flatten and are independent of the frequency applied—widens as the molecular weight of the sample increases beyond M_c. The samples exhibiting lower molecular weights do not participate in entanglements as it results from the linear dependence between both G' and G'' versus ω. $G°_N$ is found to be $(1 \pm 0.2) \times 10^6$ Pa. Since the networks were prepared in solution, G_E (the effective contribution of entanglements) should decrease proportionally to v_{2c}^2:

$$G_E = G°_N v_{2c}^2 \tag{1}$$

v_{2c} being the polymer volume fraction at the "nascent state".

Calculation of the Structural Parameters. We have used the Miller–Macosko theory to determine the number of active chains ν and the number of active junctions μ. Equations relating the sol fraction w_s—determined experimentally—to the extent of reaction (p) have been established in a previous publication.[2] The particular case involving a difunctional precursor reacting with a mixture of species exhibiting different functionalities has been treated.[2]

Rubber Elasticity. Rubber elasticity theories aim at establishing the relationships between the macroscopic elastic behavior of the network and its molecular structure. Despite the abundant literature existing in this domain—implying a great variety of approaches, models, and concepts—the calculation of the elastic free energy change upon straining a rubbery sample is still a matter of controversy. The various approaches agree however in considering that the free energy of deformation includes two contributions: the first corresponds to the "phantom-like" behavior, and the second arises from the topological interactions between the network chains. A number of theoretical models have been proposed to account for this additional contribution, usually referred to as the entanglement effect. In the limit of small strains, it is generally accepted that the topological interactions not only restrict the free fluctuations of the junctions[6,7] but also act as additional physical junctions. This approach, first suggested by Langley and Graessley,[8,9] has the advantage of taking into account long-range topological interactions between the chains. As the entanglements that have been trapped during the cross-linking reaction are not able to relax within the limit of small strains, they will simply add to the modulus. In that case, the modulus can be expressed as

$$G = (\nu - h\mu) + G°_N T_e \tag{2}$$

h is an empirical parameter related to the mobility of the junctions, which can be connected[10] to the parameter ν_2 of Flory's model. In the absence of entanglements, eq 2 stays within the limits of the two classical theories of elasticity: "phantom" and "affine". If h tends to 1 (free fluctuations of the junctions), the modulus converges to the phantom prediction:

$$G = (\nu - \mu)RT \tag{3}$$

If these fluctuations are fully suppressed ($h \rightarrow 0$), this model predicts an affine behavior:

$$G = \nu RT \tag{4}$$

T_e is the proportion of topological interactions trapped during the cross-linking reaction, and G_E is closely related to the plateau modulus, $G°_N$, as specified above.

Modulus of Networks Prepared in Solution and Swollen to Equilibrium. If V_0 is the volume of the network formed, and v_{2c} the polymer volume fraction in the "nascent" state, the modulus of a gel swollen to equilibrium according to the Langley–Graessley model is given by

$$G = [(\nu_e - h\mu_e)RT + G_E T_e] v_2^{1/3} v_{2c}^{-1/3} \tag{5}$$

ν_e and μ_e correspond to ν/V_0 and μ/V_0 and are the number of elastic chains and the number of junctions per unit volume in the nascent state, respectively. Derivation of this equation taking into account both network synthesis from a solution and swelling

Table IV
Structural Parameters of a Series of Poly(dioxolane) Gels Prepared from Seven Different PDXL Precursors

M_n	w_s[a]	v_{2c}	p[b]	ν_0[c]	$A_{f,0}$[c]	ν[c]	μ[c]
1025	2.1	0.367	0.88	0.300	0.097	0.207	0.076
1700	2.5	0.339	0.87	0.193	0.062	0.128	0.048
1750	2.8	0.339	0.86	0.189	0.061	0.122	0.046
2950	3.4	0.315	0.85	0.115	0.037	0.071	0.027
4320	3.0	0.307	0.86	0.081	0.026	0.052	0.019
6130	4.2	0.302	0.84	0.059	0.019	0.034	0.013
7910	4.9	0.300	0.82	0.046	0.015	0.025	0.010

[a] Percent extractable polymer from network. [b] Conversion attained upon network formation. [c] In moles/liter.

to equilibrium has been presented elsewhere.[2]

Expressions for the elastic moduli of the phantom and affine models can be written as

$$G_{\text{affine}} = \nu_e R T v_2^{1/3} v_{2c}^{-1/3} \tag{6}$$

$$G_{\text{phantom}} = (\nu_e - \mu_e) R T v_2^{1/3} v_{2c}^{-1/3} \tag{7}$$

Network Parameters. Any attempt to relate the network structure to the modulus requires a precise knowledge of the parameters ν and μ. Since no techniques for the direct investigation of networks are available, these parameters can only be estimated from theoretical predictions such as the gelation theory of Flory[11] and Stockmayer,[12] the cascade theory,[13] the rate theory,[14] and the recursive branching theory of Miller and Macosko.[15] We have chosen the Miller–Macosko theory for the determination of the structural parameters of our networks. Two criteria have been considered in selecting this approach rather than the others: the mathematical expressions are easy to handle and there is a good agreement between the extent of reaction predicted by this theory and the experimental value at the gel point. More details will be published in a forthcoming paper.[16] Assuming the absence of cyclic structures in the gel as well as in the sol, a simple relation can be established between the sol fraction (w_s) and the extent of reaction (p). Using computer simulation, Eichinger et al.[17] have recently pointed out that the Miller–Macosko treatment underestimates the extent of reaction in the gel by as much as 3–8%. Eichinger has attributed this discrepancy to the presence of loops in both the sol and the gel fractions. Such loops are ignored in the recursive branching theory. The actual extent of reaction is thus to be increased, according to Eichinger, on account of cyclization effects. It could be answered that the differences generally observed are within the margin of errors.

These differences might however become important in network samples prepared at high dilution and/or from small molecular weight precursor polymers. Eichinger's demonstration would have been more convincing if the actual extent of reaction had been measured independently, say by FTIR. As we have prepared our own samples at moderate concentration $v_{2c} \simeq 0.33$, the drawbacks underlined by Eichinger should have only a minor effect on the actual values of the cycle rank $\xi = \nu - \mu$. The equations for calculating the extent of reaction p from the soluble fraction w_s and those yielding ν, μ, and T_e were established in a previous paper.[2]

3. Results and Discussion

Since the actual parameters of the network can be easily calculated by using the recursive branching theory,[15] it is of interest to compare the moduli originating from phantom and affine predictions with the experimental modulus. The theoretical values are calculated according to expressions 5 and 6. Both v_{2c}, the polymer volume fraction of the network in the nascent state, and v_2, the polymer volume fraction at swelling equilibrium, result from measurements of the swelling degree. Two parameters have been varied upon preparing our PDXL networks: (i) the average length of the precursor chains, and (ii) the concentration at which cross-linking took place.

Influence of the Length of the Elastic Chains. A series of seven gels were prepared from PDXL precursors of molecular weights extending from 1000 to 9000. The gels were swollen to equilibrium in dioxane, and their mechanical properties were determined. Experimental and theoretical moduli (calculated from the structural parameters listed in Table IV) are plotted vs the molecular weight of the elastic chains for swollen networks prepared at almost the same polymer volume fraction v_{2c} (Figure 2). Another possible representation is the variation of the moduli as a function of v_2 (Figure 3). From both plots it appears that the behavior experimentally observed is intermediate between that of the affine and phantom models. For the networks involving short elastic chains the moduli are close to those predicted for the phantom model; however, as the chains become longer, the values arising from the affine model become more in agreement with the moduli measured.

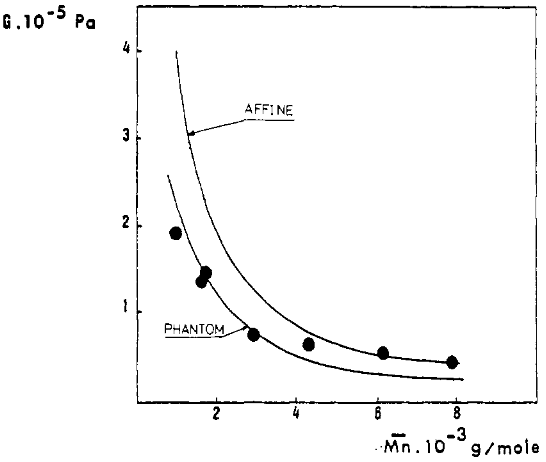

Figure 2. Dependence of the modulus (G) on the length of the elastic chains. The experimental points are represented by filled circles.

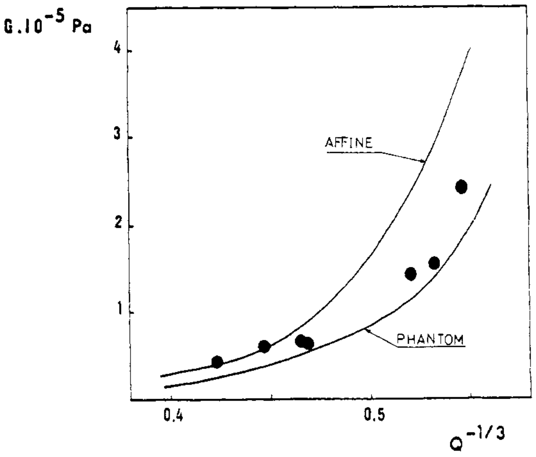

Figure 3. Modulus (G) as a function of the polymer volume fraction ($Q^{-1/3} = v_2$) for networks prepared at almost the same polymer volume fraction in the nascent state (v_{2c}). (●) Experimental points.

Influence of the Volume Fraction of Polymer in the Nascent State on the Mechanical Properties. Five

Table V
Structural Parameters of the Networks: Influence of the Volume Fraction of Polymer Segments v_{2c} upon Cross-Linking[a]

v_{2c}	w_s	p	ν_0	$A_{f,0}$	ν	μ
0.173	2.8	0.86	0.098	0.032	0.064	0.024
0.294	2.3	0.87	0.167	0.054	0.113	0.042
0.339	2.5	0.87	0.193	0.062	0.128	0.048
0.496	1.7	0.89	0.283	0.091	0.203	0.074
0.586	1.4	0.90	0.334	0.108	0.248	0.089

[a] Polymer precursor M_n = 1700; symbols as in Table IV.

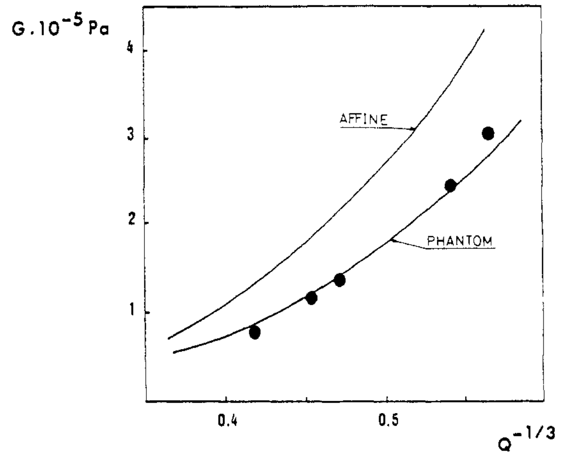

Figure 4. Modulus (G) as a function of the polymer volume fraction (v_2) for networks prepared from the same precursor (M_n = 1700) but at different v_{2c}'s ranging from 0.17 to 0.51. (●) Experimental points.

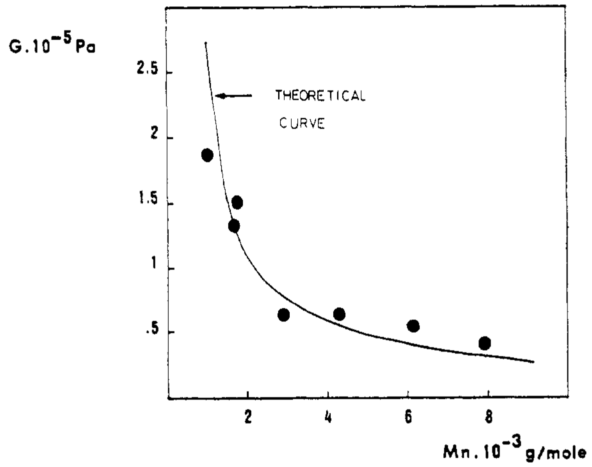

Figure 5. Modulus (G) vs molecular weight of elastically active chains. The solid curve corresponds to the modulus calculated according to eq 5, which takes into account the contribution of entanglements.

samples were synthesized starting from the same precursor (M_n = 1800) at various concentrations (Table V) and were characterized as previously. Since the elastic chains of these networks are rather short, good agreement between experimental and phantom behavior is expected based on the observation made above. These experiments were carried out in order to check whether cyclizations can be evidenced in the networks, especially in those prepared at low concentration. If the cyclizations are unduly neglected—as was done in the determination of structural parameters—the extent of reaction at the gel point should be underestimated. This should result in a large gap between calculated and experimental moduli: The presence of cyclic structures in the gel would lower the experimental modulus to such an extent that departure from the prediction of the phantom model should be important. Actually, the moduli measured are very close (Figure 4) to those calculated according to expression 7. Surprisingly, the mechanical properties of the swollen networks do not seem to depend upon the concentration at which cross-linking took place. The samples prepared at lower concentrations exhibit smaller elastic moduli, but this is mainly due to a lesser extent of reaction. In the range of concentrations examined, defects such as loops—if they exist—are of minor importance.

Estimation of the Entanglement Effect. As mentioned above, it is now accepted that in real networks two additional contributions to the elastic free energy have to be taken into account in addition to the phantom behavior: that arising from the limitation to the free fluctuations of junction points, and the entanglement effect. The problem is to quantify the extent of each contribution to the increase of F.

The effect of entanglements can be measured independently on linear samples, and the onset (M_c) of these long-range interactions is displayed upon plotting viscosity versus molecular weight of the samples (Figure 1). In our case the spacing between entanglements (M_c)—determined from oscillatory shear measurements—is estimated around 2200. For networks prepared from short precursor chains ($M < M_c$) the deviation from phantom behavior, if any, is to be attributed solely to the limitation of junction fluctuations, the entanglements being nonexistent. It can be seen from Figure 2 that the experimental moduli and those predicted by the phantom model are very close for these gels, which can be interpreted by the absence of restrictions to the free fluctuations of junctions. The same behavior (h = 1) can be expected from networks involving longer elastic chains ($M > M_c$) since they exhibit even higher swelling degrees. Though the junctions can be considered free of any constraint, the interactions between chains must exist. Figure 2 displays the variation of moduli vs the molecular weights of the precursor. It evidences the entanglement effect. Departures of the experimental moduli from the phantom predictions arise beyond M_c. This ascertains the presence of entanglement. Their contribution to the elastic properties is however low, since the cross-linking reaction has been carried out in a solvent. The additional term $G_{\mathrm{E}}T_{\mathrm{e}}$—with $G_{\mathrm{E}} = G^{\circ}{}_{\mathrm{N}}v_{2c}{}^{2}$—arising from entanglements leads to a good fit with experimental data (Figure 5). The Langley–Graessley concept thus allows one to explain the elastic behavior of networks in the domain of small strains.

Swelling of PDXL Networks. The interpretation of swelling data is often a matter of controversy. It is usually agreed that the Gibbs free energy of swelling is the sum of the free energy of mixing and the elastic free energy (Flory–Rehner hypothesis). However, the calculation of this latter term differs depending upon the theory of rubber elasticity chosen. The conclusions drawn from comparison with experimental data are thus affected by the choice of the model. Recently, the validity of the Flory–Rehner hypothesis has even been questioned.[18] The interpretation proposed here aims at staying independent of any particular model for the F_{elast} calculation, but considering the Flory–Rehner hypothesis to be valid.

Table VI
Determination of the Flory–Huggins Interaction Parameter χ_{12} for Poly(dioxolane) Networks Swollen in Dioxane

M_n	v_{2c}	v_2	$G_{exp}/(RTv_2^{1/3}v_{2c}^{-1/3})$	χ_{12}
1025	0.367	0.164	0.102	0.378
1750	0.339	0.153	0.082	0.379
2950	0.315	0.103	0.038	0.366
4320	0.307	0.101	0.039	0.352
6130	0.302	0.090	0.034	0.332
7910	0.300	0.076	0.025	0.331
1700	0.586	0.236	0.170	0.442
1700	0.496	0.208	0.130	0.430
1700	0.339	0.142	0.074	0.369
1700	0.294	0.128	0.064	0.349
1700	0.173	0.102	0.039	0.339

In the expression of F_{elast} the term differing from one theory to another is the front factor. As an example, in the junction fluctuation model,[6,7] the values of A and B in the expression of F_{elast}

$$F_{elast} = A\nu_e/2(\lambda_x^2 + \lambda_y^2 + \lambda_z^2) - B\nu_e \ln(\lambda_x\lambda_y\lambda_z)$$

are respectively $(f - 2)$ and 0 if the phantom network model applies and 1 and $2/f$ in the case of an affine network (f is the number-average functionality of the network cross-links). At swelling equilibrium, the following equation can be obtained upon using the Flory–Erman expression for the elastic contribution:

$$\ln(1 - v_2) + v_2 + \chi_1 v_2^2 = -\frac{\nu - \mu}{V_0} V_1 v_2^{1/3}\left[1 + \frac{\mu}{\nu - \mu} K(v_2^{-2/3})\right] \quad (8)$$

χ is the interaction parameter, K is a complex function of κ measuring the severity of the entanglement constraints and of ξ, which takes into account the nonaffine transformation of the domain of constraints, V_1 is the molar volume of the solvent, and V_0 is the volume of the gel at the reference state. For a phantom network, $\kappa = 0$ and $K(\lambda^2) = 0$, expression 8 reduces to

$$\ln(1 - v_2) + v_2 + v_2^2\chi_1 = -\frac{V_1}{V_0}(\nu - \mu)v_2^{1/3} \quad (9)$$

For a network that behaves affinely, $\kappa = \infty$, $K(\lambda^2) = 1 - \lambda^{-2}$, expression 8 can be written as

$$\ln(1 - v_2) + v_2 + v_2^2\chi_1 = -\frac{V_1}{V_0}(\nu v_2^{1/3} - \mu v_2) \quad (10)$$

The term μv_2 can be neglected and eq 10 becomes

$$\ln(1 - v_2) + v_2 + v_2^2\chi_1 = -\frac{V_1}{V_0}\nu v_2^{1/3} \quad (11)$$

As it cannot be decided a priori which theory—affine or phantom—applies to our networks and since the values of the parameters are still unknown, the use of eq 9 or 11 to interpret our swelling data would be inappropriate. The uncertainty concerning $(\nu - \mu)$, we have chosen to calculate this term from our experimental data. In expression 5, the term in brackets corresponds to $G/(RTv_2^{1/3}v_{2c}^{-1/3})$ and it can be calculated since all the other parameters are known. After this term is reintroduced into eq 9 in place of $(\nu - \mu)$, one obtains

$$\ln(1 - v_2) + v_2 + v_2^2\chi_1 = -\frac{V_1}{V_0}\frac{G}{RT}v_{2c}^{1/3} \quad (12)$$

χ may be calculated through eq 12. Table VI lists the values of χ determined for each sample. A consequence of this interpretation—based on the Flory–Rehner hypothesis—is that a relation is found between the interaction parameter and the volume fraction of polymer v_2 in the swollen state. Upon plotting χ as a function of v_2, one gets a linear variation (Figure 6), consistent with investigations on linear polymers establishing χ_{12} to be concentration dependent.

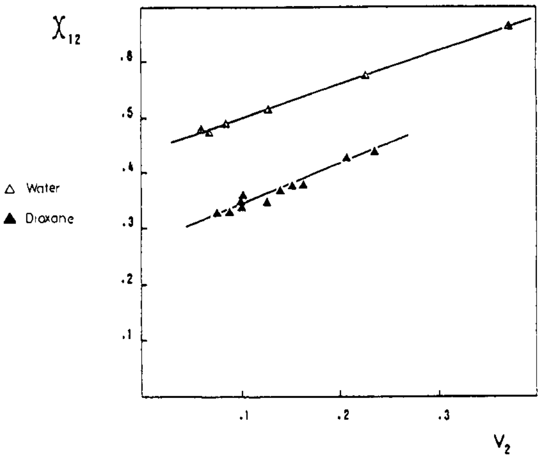

Figure 6. Plot of χ_{12} vs v_2 (polymer volume fraction).

Table VII
Determination of the Flory–Huggins Interaction Parameter χ_{12} for Poly(dioxolane) Networks Swollen in Water

M_n	v_{2c}	v_2	$G_{exp}/(RTv_2^{1/3}v_{2c}^{-1/3})$	χ_{12}
1025	0.367	0.373	0.101	0.666
1750	0.339	0.227	0.076	0.574
2950	0.315	0.129	0.040	0.516
4320	0.307	0.086	0.032	0.488
6130	0.302	0.069	0.024	0.476
7910	0.300	0.060	0.017	0.478

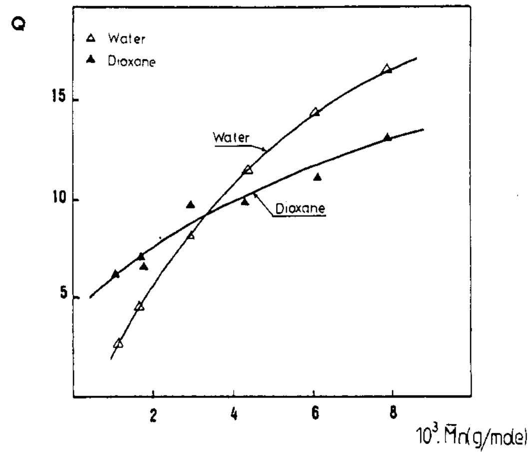

Figure 7. Equilibrium swelling degrees of six PDXL gels in dioxane and in water as a function of the molecular weight of the elastic chains.

Elastic and Swelling Properties in Water. The equilibrium swelling degrees of our various samples in water as well as the corresponding moduli are listed in Table VII. The hydrophobic nature of the cross-linking agent is evidenced. The networks involving shorter PDXL chains—and consequently a larger proportion of hydrophobic urethane junctions—exhibit swelling ratios lower than those measured in dioxane. Conversely, the gels with large elastic chains swell more in water than they do in dioxane (Figure 7). We have calculated the parameter χ_{12} (Table VII), characterizing the water–gel interactions by the same procedure as that described above. A linear dependence of χ_{12} vs v_2 is found (Figure 6).

From this plot it appears that water is worse than dioxane as swelling agent. In the case of short-chain

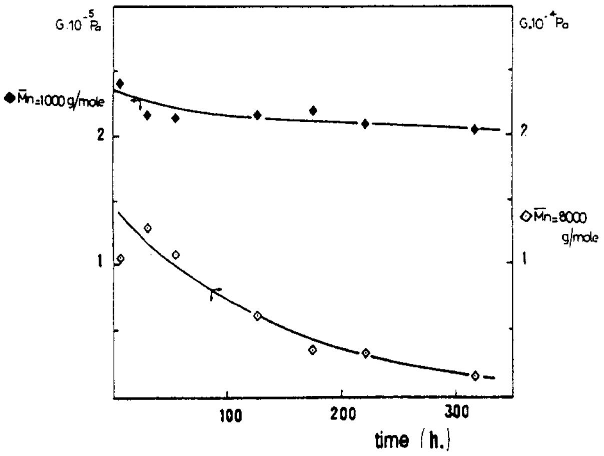

Figure 8. Plot of G vs time for two PDXL gels swollen to equilibrium in acidic aqueous medium.

networks, water can even be considered to be a poor solvent, as is evidenced by the turbid aspect of these swollen samples.

More astonishing is the behavior of networks involving long PDXL chains. As mentioned above, they swell more in water than in dioxane. This apparent contradiction might be explained by the hydrophobic nature of the urethane linkages. Below a given volume fraction of polymer these junction points tend to aggregate, inducing heterogeneities in the network. This could possibly account for the enhanced swelling observed in water.

Controlled Degradation of PDXL Networks in Acidic Media. Poly(dioxolane) belongs to the family of polyacetals, which are known to be unstable in acidic media. We have followed the hydrolysis of two PDXL networks in aqueous acidic media by measuring the elastic moduli after various reaction times. The two networks originate from precursor chains of M_n = 1000 and M_n = 8000, respectively. The modulus is plotted versus the time of immersion in the acidic medium (Figure 8). The sample involving long elastic chains—which exhibits the higher swelling degree—undergoes rapid degradation. For the network constituted of short elastic chains, the elastic modulus decreases only slightly after 2 weeks under the same conditions. To account for this result two factors are to be considered: the higher concentration of H$^+$ in the sample exhibiting the larger swelling degree, and the higher proportion of acetal functions in that sample.

4. Conclusion

Three different problems have been examined in this investigation of poly(dioxolane) networks obtained by end-linking: (i) the elastic behavior of these gels when swollen to equilibrium, (ii) their swelling properties in dioxane and in water, respectively, and (iii) the degradability of these polyacetals in acidic aqueous media.

The results obtained in the domain of rubber elasticity within the limits of small strains are well described by the Langley–Graessley model. The short-range interactions, limiting the fluctuations of junctions, have been shown to be negligible. The experimental moduli of these samples are in good agreement with those predicted by the phantom model. Conversely, the long-range topological interactions (trapped entanglements)—expected to play a role in networks involving longer elastic chains—have been found to contribute to the elastic moduli.

The swelling data have been analyzed within the framework of the Flory–Rehner hypothesis. The interpretation proposed is not model dependent, and a linear dependence of χ_{12} versus v_2—the reciprocal of the swelling degree—is evidenced.

The chemical instability of these networks when swollen in acidic aqueous medium has been discussed. Applications of those materials as biomedical devices can be foreseen.

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