of the polymer. The asymptotic energy storage increases with G, i.e., with decreasing chain stiffness. In the extensional flow case, the average monomer-flow interaction is expected to increase faster than linearly with the strain rate since it is proportional to $\langle r^2 \rangle$ which increases rapidly with it.[10] Thus the asymptotic regime in $\ln F$ can be reached for moderate values of the applied strain rate.

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(1) More appropriately one should refer to free-energy storage. We shall use the latter term in the following.
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Spontaneous and Rapid Polymerization of Plasma-Exposed Monomer Crystals in the Liquid Phase

A plasma is a partially ionized gas composed of electrons, ions, radicals, and photons spanning a wide range of energy. Among them electrons particularly generated by the glow-discharge plasma gain energy from an imposed electrical field and lead to the formation of a host of chemically reactive species, some of which become precursors to the plasma polymerization as well as plasma-initiated polymerization.[1,2]

We report here an interesting polymerization process in which plasma is used to generate the active species with very long life on the crystal of water-soluble monomers. The active species thus formed cannot initiate the polymerization at all as long as the monomer remains in the solid state. However, when the monomer crystal is allowed to dissolve by introducing water in vacuo, it can initiate the polymerization very rapidly and gives a polymer with extremely high molecular weight.

Thus, once the monomer crystal has been exposed to the plasma beforehand for 60 s or less, one can obtain the polymer in situ only by dissolving the monomer crystal in water (or acid solution in some cases). This polymerization process was referred to as plasma-initiated solvopolymerization.

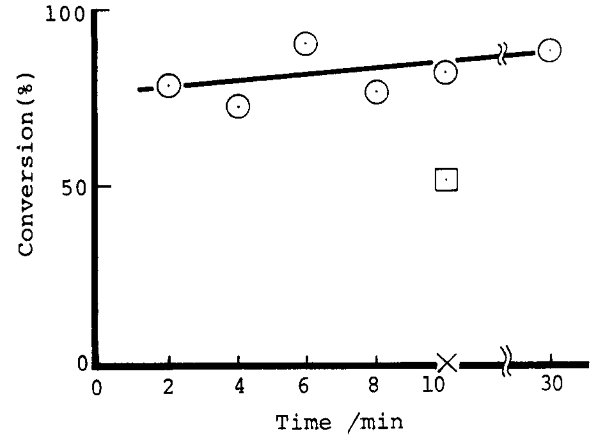

Figure 1. Monomer conversion-postpolymerization time profile for the polymerization of AMPS. AMPS 1.5 g, 4 mL of water (⊙), Me$_2$SO (□), or DMF (×) was added to the AMPS crystal immediately after plasma exposure. Postpolymerization, 25 °C.

The experimental apparatus and procedure used in the present investigation are similar to those reported previously,[3-6] i.e., 0.5-1.5 g of purified monomer crystal was evacuated several times in a 25-mL Kjeldahl flask under 1.0-0.1 Pa. The flask was inserted between a pair of parallel-plate electrodes connected to a plasma generator operating at 13.56 MHz. A glow discharge was initiated in the gas phase for 60 s at 100 W.

Four milliliters of water (or aqueous acid) previously degassed was then introduced in vacuo into the flask containing the monomer crystal, dissolved by shaking vigorously, and postpolymerized for 2-10 min at 25 °C. Obtained polymer solution was precipitated in a large amount of poor solvent, dried in vacuo, and weighed to determine the percent conversion. In some cases the plasma-exposed monomer crystal was allowed to stand for several days or weeks in vacuo, dissolved in water, and postpolymerized for 10 min.

The polymerization of the plasma-exposed crystal took place only by dissolving in water and no polymerization occurred in the crystalline state at all. Once water was introduced, the rate of polymerization was very high and appeared to occur almost simultaneously with dissolution in water. Figure 1 shows conversion-postpolymerization time profile for the polymerization of 2-acrylamido-2-methylpropanesulfonic acid (AMPS). It is seen that the polymer is obtained with 80% conversion only 2 min after water was introduced. Polymerization occurred also by dissolving in dimethyl sulfoxide (Me$_2$SO), but no polymer was obtained in dimethylformamide (DMF) in analogy with plasma-initiated solution polymerization in DMF.[7,8] The active species generated in the AMPS crystal had very long life. Polymerization occurred even when the plasma-exposed crystal was allowed to stand for several months in vacuo and then dissolved in water and postpolymerized for 10 min. The polymer yield decreased only slightly (Figure 2a). However, when the plasma-exposed AMPS crystal was left in aerobic condition, the polymer yield decreased from 80% to 50% in 10 h, which later remained constant (Figure 2b).

We reported previously that the polymers obtained by the plasma-initiated polymerization are un-cross-linked soluble polymers[3,4] having extremely high molecular weight as large as 3×10^7.[9] The molecular weight of polymers obtained by this method was also very high. For example, intrinsic viscosities of AMPS polymers obtained after 2 and 6 min of postpolymerization showed 18.0 and 16.5 dL/g, respectively, in 0.1 mol/dm^3 aqueous NaCl solution

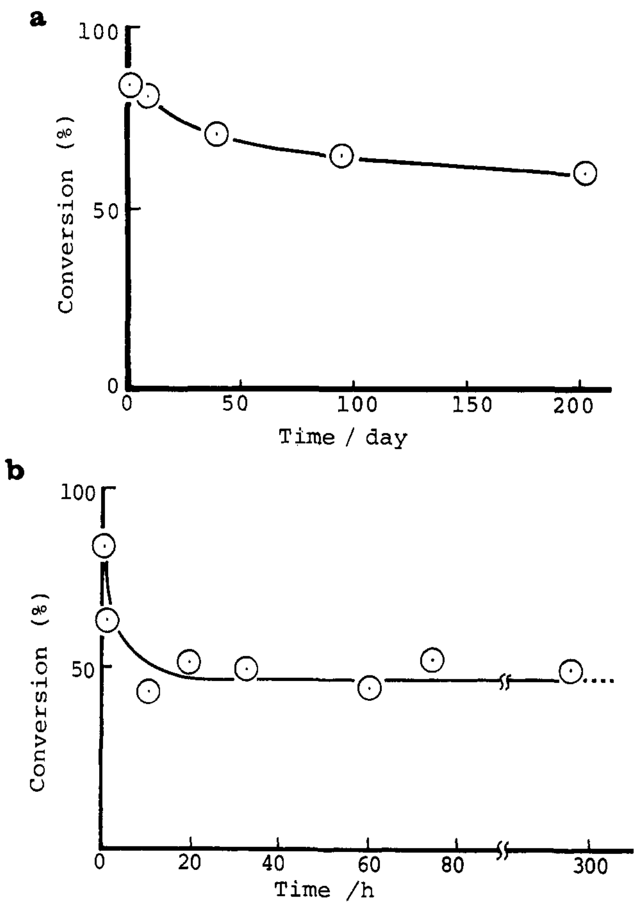

Figure 2. (a) Time dependence of monomer conversion when the plasma-exposed AMPS crystal was allowed to stand in vacuo. Postpolymerization: 10 min, 25 °C. AMPS 1.5 g, water added (4 mL). Abscissa indicates the duration until water was added. (b) Time dependence of monomer conversion when the plasma-exposed AMPS was allowed to stand in aerobic conditions. Experimental conditions are identical with those in (a).

at 30 °C. The sample which was allowed to stand for 6 days in vacuo after plasma exposure and postpolymerized for 10 min showed 14.5 dL/g. Since no viscosity–molecular weight relationship is established for the given polymer, molecular weight cannot be determined at present from these data. GPC measurement in water, however, showed a part of peak tailing to lower molecular weight near 21.5 min, from which molecular weight could roughly be estimated as 10^7 or higher.[8]

Crystalline acrylic monomers having no ionizable group such as acrylamide, methacrylamide, *N*-hydroxymethyl methacrylamide, and diacetone acrylamide did not polymerize by addition of water. However, introduction of sulfuric or hydrochloric acid instead of water resulted in an effective polymerization. An interesting feature here is that the rate of polymerization increased in proportion to the hydrogen ion concentration of the acid introduced. The result is shown in Figure 3.

We already reported that no vinyl monomers other than acrylates and methacrylates were subject to the plasma-initiated polymerization.[1,10] Consistent with this, crystals of sodium salts of styrenesulfonic acid and vinylsulfonic acid were not polymerized by the given method.

The mechanism of this unique polymerization process is not fully understood. However, taking into account the polymerization behaviors described above as well as those of plasma-initiated polymerization systems already reported,[7,8,11] the anion radical generated at the surface of crystalline monomer is assumed to be the primary active species, which then changed to the free radical by the reaction with hydrogen ions. The speculated process of the polymerization was elucidated as follows:

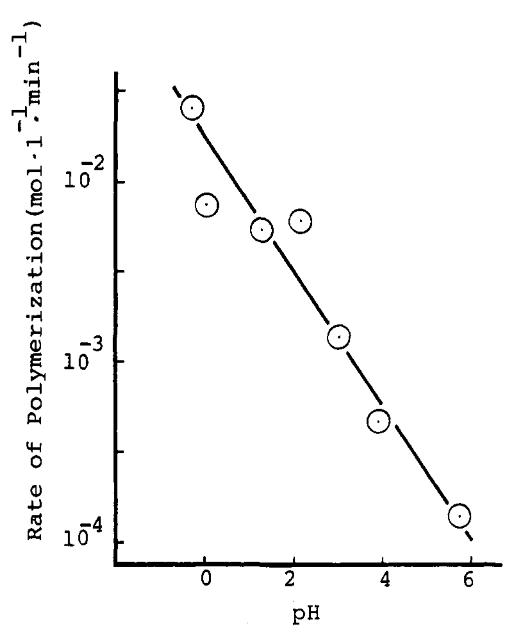

Figure 3. pH dependence of the rate of polymerization of acrylamide. Acrylamide, 0.52 g; postpolymerization, 25 °C. Four milliliters of sulfuric acid with different normalities was added immediately after the plasma exposure.

$$e^- + M_s \longrightarrow M_s^-\cdot$$

$$M_s^-\cdot + H^+ \xrightarrow{k_i} HM^* \qquad R_i = k_i[M_s^-\cdot][H^+] \qquad (1)$$

$$HM^* + M_l \xrightarrow{k_p} M_n^* \qquad R_p = R_i[M_l]$$

$$= k_i[M_s^-\cdot][H^+][M_l] \qquad (2)$$

$$\log R_p = \log k_i + \log [M_s^-\cdot] - \text{pH} + \log [M_l] \qquad (3)$$

$$= K - \text{pH} \qquad (4)$$

where e^-, M_s, and M_l are the concentration of energetic electrons in the plasma, effective concentration of solid monomer, and monomer concentration dissolved in water or acid, respectively. Since the amount of anion radical formed on the monomer crystal $[M_s^-\cdot]$ is constant under constant plasma condition, the rate of polymerization is simply expressed as a function of pH as in eq 4 which is consistent with the experimentally obtained result in Figure 3. A UV-assisted mechanism is equally possible to the electron–anion mechanism since plasma is rich in UV and vacuum-UV photons. Therefore, we carried out UV irradiation using 400-W high-pressure mercury lamp for 60 s from 5-cm distance to an evacuated optical quartz cell of 10-mm path length, in which 0.75 g of AMPS crystal was placed. However, only 1.2% conversion was obtained after 10 min postpolymerization in water, indicating that direct action of energetic electron–molecule reaction occurring in the plasma[12–14] plays an essential role for the initiation.

Registry No. AMPS, 15214-89-8; acrylamide, 79-06-1.

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Solvent vs. Segment Orientation in Strained Swollen Elastomeric Networks

Deuterium NMR (DMR) has emerged as a valuable technique for investigating orientational order generated in uniaxially strained rubbers. The methodology exploits the observation of residual quadrupolar interactions (usually in the form of a resolved, quadrupolar splitting) which may be related to the degree of induced order in the rubber. In 1981 Deloche and Samulski[1] used deuterated swelling agents at low concentrations (solvents such as benzene-d_6, chloroform-d_1, etc.) as DMR probes in elongated rubbers and inferred that *both* the solvent probe and the polymer segments experience short-range orientational correlations.[2] Solvent quadrupolar splittings unequivocally demonstrate the existence of the orientational coupling between solvent molecules and ordered segments of the deformed chains. Extensions of such DMR measurements to labeled networks enabled direct studies of the chain segment behavior.[3,4] More recently, investigations of segment (and probe) quadrupolar interactions have been shown to be related to network cross-linking density and to be attenuated by swelling the networks.[5] This dependence on network characteristics strongly supports the initial proposal that short-range segment–segment (and solvent–segment) correlations must be included in a comprehensive description of elastomeric networks.[1] Here we use DMR to contrast segmental and solvent probe orientational order in well-defined poly(dimethylsiloxane) networks. This study gives direct insights into the nature of the orientational field that both probe molecules and chain segments experience in deformed networks.

Identical tetrafunctional end-linked poly(dimethylsiloxane) networks were prepared as described previously[6,7] (the molecular weight between crosslinks $M_n = 23\,000$; the molecular weight distribution is 1.6). Network formation was carried out at a polymer volume fraction of $V_c = 0.71$. One network, PDMS(D), contains a known fraction (~20%) of perdeuterated chains: $(\text{–Si(CD}_3)_2\text{–O–})_n$. The second network, PDMS, is unlabeled. These two samples, PDMS(D) and PDMS, were swollen with benzene and benzene-d_6, respectively. Network swelling and elongation were performed as indicated earlier.[1,3,5] DMR spectra were obtained with a CXP-90 Bruker spectrometer operating at 2 T; the field $\mathbf{B}_0$ is normal to the principal strain direction **d** of the uniaxially deformed network.

Typical quadrupolar splittings for benzene-d_6 and PDMS(D) are shown in the DMR spectra in Figure 1 at the same extension ratio $\lambda = L/L_0 = 1.42$. The volume fraction of polymer in the swollen networks is $\phi = 0.92$. The resolved doublet of the solvent probe is characteristic of that obtained with a variety of labeled swelling agents in various elastomer networks.[1,5] One of the primary sources of the lack of resolution in the PDMS(D) spectrum can be attributed to a superposition of spectra originating from a distribution of chain lengths between junctions:[4,8] For a given λ, classical descriptions[9] of rubber elasticity indicate that higher orientational segmental order will be exhibited by the shorter chains.

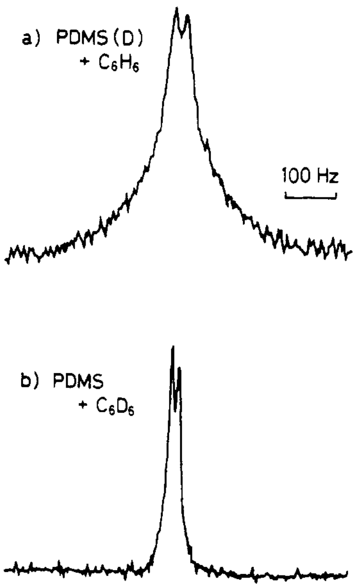

Figure 1. DMR spectra of (a) perdeuterated poly(dimethylsiloxane) chains in a network PDMS(D) swollen with benzene and (b) benzene-d_6 in an unlabeled PDMS network. In both samples the polymer volume fraction $\phi = 0.92$ and the elongation ratio $\lambda = 1.4$.

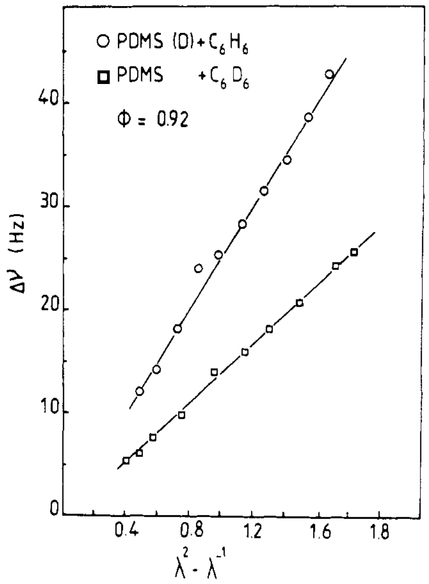

Figure 2. Solvent probe and polymer quadrupolar splittings $\Delta\nu$ vs. $\lambda^2 - \lambda^{-1}$.

Figure 2 shows the quadrupolar splittings of the solvent, $\Delta\nu_s$, and of the polymer, $\Delta\nu_p$, vs. $\lambda^2 - \lambda^{-1}$ for both networks in the small deformation limit ($\lambda \leq 2$). As reported earlier,[1,3] both $\Delta\nu_s$ and $\Delta\nu_p$ are linear in this strain function; at the same λ the observed ratio $\Delta\nu_s/\Delta\nu_p = 0.56$. In the following we examine the implications of the order of magnitude equivalence of solvent and chain segment quadrupolar splittings in comparable networks at the same degree of swelling.

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