Structure and Surface Properties of Diaminocyclohexane Plasma Polymer Films

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SYNOPSIS

Plasma polymers of three isomers of diaminocyclohexane (DACH) were deposited on polyethylene, SiO_2, and mica at 20°C. The deposition rate was measured as a function of plasma density and power; a maximum was observed in the latter function. The deposition rate was highest for the monomer with the highest flow rate. The film refractive index was observed to increase with both power density and the degree of fragmentation in the plasma. Film composition was measured by elementary analysis, and was found to be almost identical for each of the three isomers; a mechanism for the polymerization reaction is proposed. The percentage of primary amino groups decreased with increasing power density and with film thickness. Surface force measurements of the thickness and refractive index agreed well with the corresponding ellipsometry values in dry air, and an adhesive force, independent of power density, was measured. When the film was exposed to water vapor, it swelled considerably and the adhesion was determined by capillary forces. Associated with swelling, at high power, was an extremely regular 2-ply rope pattern of protruding material. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Since amino groups are suitable reactants in many derivatizing reactions, aminofunctionalization of surfaces is of interest in several industrial applications, such as adhesion of coatings and the tailor-making of surfaces for blood or tissue contact.

The authors have developed a method to aminofunctionalize surfaces by adsorption and partial crosslinking of a branched poly(ethylene imine).[1] The advantage of this technique is that the surface density of amino groups is large and can be controlled by the solution pH during adsorption, by the degree of branching, and by the molecular weight of the poly(ethylene imine) chosen. However, adhesion was sometimes a serious drawback, since the film was attached to a surface by multiple physical bonds (primarily H-bonding, double layer forces, and hydrophobic interaction), which could be broken by a change in the pH or ionic strength of the solution or by changing the polarity of the solvent.

In this article, we describe a procedure to functionalize the surface of poly(ethylene), SiO_2, and mica, by means of the plasma polymerization of diaminocyclohexane. Interaction properties and swelling of the film were studied with a surface force apparatus. The amino groups in the plasma polymer film were quantified by means of Electron Spectroscopy for Chemical Analysis (ESCA). The accessibility and reactivity of the amino groups were studied by means of a tagging reaction with perfluoro benzaldehyde. Based on the compositions of the films, as derived from ESCA and ATR–FTIR analysis, a tentative polymerization mechanism for 1,2-diaminocyclohexane in the plasma is presented.

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MATERIALS AND METHODS

Chemicals

1,2-Diaminocyclohexane (DACH) and 1,4-DACH were purchased from Aldrich and 1,3-DACH was obtained from CTC Organics, USA. All products were mixtures of cis- and trans isomers and were used without further purification. Perfluorobenzaldehyde (PFB) was of reagent grade from Fluka. Sodium cyano borohydride was from Aldrich Chemie, Germany.

Plasma Polymerization

A tubular reactor (I.D. = 15 cm, L = 65 cm), with copper-band electrodes, was used. The frequency of the RF generator was tuned in at the range of 3–400 kHz. The plasma system has been described in detail elsewhere.[2]

Plasma polymer films were deposited on five different substrates:

1. Freshly cleaved Mica (Mica Supplies, UK) was used for quantitative ESCA analysis and surface force (S.F.) measurements.
2. Silicon wafers (Wacker Chemie, Germany) were used for ellipsometry studies.
3. Germanium (Harrick Scientific Corp., USA) was used for FTIR analysis using attenuated total reflection (ATR).
4. Filler-free, transparent, 1 mm thick, low-density polyethylene (LDPE), with density δ = 0.93 g/cm^3 at 23°C, was a gift from NOAX AB, Stockholm, Sweden.
5. A gold electrode plate, on top of the quartz crystal microbalance (QCM), was used for measuring deposition rates.

All samples (1–4) were 10 × 14 mm in size. They were attached with a double-sided Scotch tape to a plate of stainless steel, which was fixed on a steel rod with variable length. The rod length was adjusted so that the sample was placed 15 cm below the lower electrode.

The DACH isomers were placed in an 100-mL flask, connected to the reactor by means of teflon tubing (I.D. = 2 mm), which was sealed with an O-ring connection. The vapor was allowed to flow without control into the reactor at room temperature. The 1,4-DACH was heated to 30°C before entering the chamber. The flow rate, F, was determined by recording the pressure increase while closing the throttle valve. It was F = 2.6 SCCM for 1,2-DACH,

0.75 SCCM for 1,3-DACH, and 0.22 SCCM for 1,4-DACH. The pressure in the reactor before plasma ignition was adjusted to approximately 2.4 Pa by adjusting the pumping capacity with a throttle valve. Five sets of samples were prepared using W = 5, 7.5, 10, 20, and 80 Watts (for surface force measurements 40 and 60 Watt samples were also prepared), with fixed flow rates as specified above. The energy input in the reactor is described by the composite parameter W/FM (J/kg), where M denotes the molecular weight of DACH, and W and F are defined above. The pressure change was continuously monitored during plasma ignition and deposition.

Film Characterization

The elementary composition of the films was analyzed at Mikrokemi AB, Sweden. Three replicates of each isomer were analyzed.

The elementary composition of the outermost surface of the films on mica and polyethylene was determined by means of ESCA, model LH 2000 (Leybold Hereus, Germany). Scofield's relative cross sections[3] were used for calculating the stoichiometrical ratios of the elements. The number density of amino groups on mica was determined from the nitrogen $1s$/potassium $2p$, or the carbon $1s$/potassium $2p$ intensity ratio, according to the quantitative calculation procedure developed by Herder et al.[4] Deconvolution of the carbon $1s$ signal was made by using a Gaussian curve fitting program. Standard chemical shifts were taken from Gelius et al.[5] and a constant FWHM value of 1.5 eV was chosen. This FWHM value produced the best fit, but the result of the deconvolution should be regarded as indicative rather than conclusive, since the "true" chemical shifts for all the carbon species involved are not accurately known.

The content of primary amino groups in the films was analyzed by performing a derivatization reaction with PFB[6], followed by ESCA analysis of the fluorine-to-nitrogen ratio on the surface. The condition for the reaction was: 5% w/w PFB (+50 mg NaBH$_3$CN) in ethanol, 60°C, reaction time t = 30 min. Subsequently, the samples were rinsed in pure ethanol and finally in Millipore-filtered water for 60 min. The F/N ratios were then corrected for the F/N ratio for a blank sample, treated in air plasma, 10 Watts, 20 mtorr, at a gas flow of 2.5 SCCM, followed by soaking in PFB solution.

Contact angles on DACH films were measured with a goniometer, model A100 (Rame Hart, France). The scattering in the advancing contact angles was 2–3°. The receding angles were also mea-

sured and were generally 10–15° lower, but were also less reproducible (differing ±5–10° from sample to sample). We therefore measured the advancing contact angles to estimate relative changes in surface energy as a function of energy input.

The film deposition rate was measured by means of a quartz crystal microbalance (QCM) (Inficon R, MKS, Germany). The QCM measures the film thickness, d, during the deposition process from the resonance frequency change Δf of the quartz crystal, $d = k \times \Delta f$. There is, however, a debate as to whether a "true" thickness is obtained, since the calibration factor k depends on the film density, which usually is not known. Moreover, electronic disturbances from the RF plasma field may influence the measured value. However, it is the only *in situ* method available and here we have used it merely to monitor relative deposition rates and to follow its trend towards the steady state in the initial period after plasma ignition. The QCM device, with a circular capacitor surface ($\phi = 10$ mm), was placed in the reactor at the same position as that used for the sample.

Film thicknesses and refractive indices were determined for plasma films on silicon wafers with a Rudolph Research ellipsometer, Auto-ELIII. From the refractive index, N_f, and thickness, d, of the DACH film, deduced from Drude's equation,[7] the mass of the deposited film was calculated according to:

$$\text{mass (mg)} = d \times \rho = 0.1 \times M/A \, d \text{ (nm)}$$
$$\times (N_f^2 - 1)/(N_f^2 + 2) \quad (1)$$

where ρ is the film density, A is the molar refractivity, N = the number of moles per unit volume, and M is the molecular weight of the film components.[8]

Ethanol extracted material from 1,2-DACH films was analyzed with size exclusion chromatography (SEC) on an Ultrahydrogel linear gel (Waters, Millipore) with a Refractive Index detector, using polyethyleneglycol standards for molecular weight calibration.

Surface Force and Adhesion Measurements

The surface force apparatus[9,10] was also employed for the physical characterization of the 1,2-DACH film. The 1,2-DACH monomer was polymerized onto freshly cleaved mica samples, which were silvered on one side and mounted on silica discs with cylindrical curvature ($R = 2.0$ cm). The thickness of the DACH layer was measured interferometrically and the refractive index was also calculated from the

positions of the fringes of equal chromatic order.[5] The spring was then used to apply a force to separate the surfaces until the gradient of force between the surfaces became smaller than the spring constant and they jumped apart. The distance jumped can be used to obtain a value for the surface energy, γ,[9] but there is debate as to the exact formula for determining this value.[11–14] Since the mica surface deforms (the glue upon which the mica is mounted is deformable), the best approximation is probably that for deformable surfaces, that is $\gamma = F(0)/3\Pi R$, which accordingly was utilized here.

The adhesion force between a laminate, consisting of a DACH film deposited on polyethylene and a polyamide film, was also measured with an Instron apparatus. The laminate was formed by compression of the two films at 300 psi for 3 min at 100°C. A T-peel test was performed and the failure force was measured in N/m.

RESULTS AND DISCUSSION

Deposition Characteristics

Figure 1 shows the average deposition rate during the first 10 min as a function of energy input for
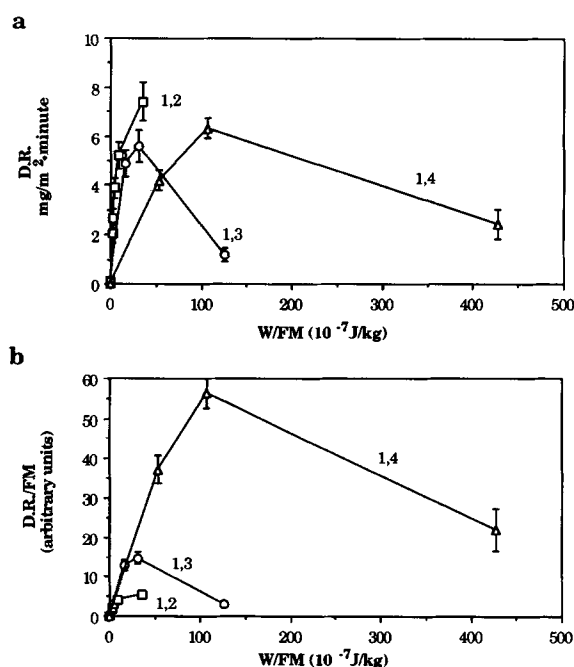
Figure 1 Average (10 min) deposition rates, DR, for DACH plasmas, as a function of W/FM, as measured with ellipsometry on SiO_2; ($\square$) 1,2-DACH, $F = 2.6$ SCCM; ($\bigcirc$) 1,3-DACH, $F = 0.75$ SCCM; ($\triangle$) 1,4-DACH, $F = 0.22$ SCCM. (a) DR vs. energy input W/FM. (b) DR/FM, normalized deposition rate, vs. W/FM.

Table I Steady State (After 10 Min) Deposition Rates, d, for DACH Plasmas Obtained by Ellipsometry[a]

W (Watts)	W/FM $(10^{-7}$ J/kg)	N_f (St. State)	d (Å/min)	A	M (g/mole)	ρ (g/cm^3)
0	0	1.46	0			
	1,2-DACH			34.69	114	1.05
5	2.3	1.54 ± 0.02	18 ± 3			1.14
7.5	3.4	1.55 ± 0.02	23 ± 3			1.16
10	4.5	1.56 ± 0.02	33 ± 3			1.17
20	9.0	1.58 ± 0.04	43 ± 4	26.15	94	1.21
80	36.0	1.75 ± 0.02	50 ± 5			1.48
	1,3-DACH			34.69	114	1.05
10	15.7	1.71 ± 0.02	32 ± 3			1.54
20	31.4	1.88 ± 0.04	31 ± 4	23.06	91	1.80
80	126.0	2.11 ± 0.02	6 ± 2			2.11
	1,4-DACH			34.69	114	1.05
10	53.0	1.62 ± 0.03	31 ± 3			1.34
20	107.0	1.64 ± 0.04	46 ± 3	24.09	92	1.37
80	427.0	2.12 ± 0.02	12 ± 3			2.05

[a] The film density, ρ, was calculated from the measured steady state N_f value and utilizing the Lorenz-Lorenz relation (ref. 6) with inserted values of molecular weight, M, and molar refractivity, A, as obtained from the elementary composition.

the three isomers obtained from ellipsometry. In the mass calculations [from eq. (1)] shown in Table I, we used M and A values, calculated from the gross formula of each DACH isomer, as obtained from elementary analysis (Table V). Table I also shows the film densities calculated from eq. (1). We have assumed that the film composition, here measured for films deposited at W = 20 Watts, is the same, regardless of plasma power, which may be a crude approximation. However, even comparatively large changes in composition result in only minor changes in A. Hence, the trend in the film density is clear; density increases with energy input in the plasma.

The deposition rate generally increases with energy input and, at the low flow rates used for 1,3- and 1,4-DACH, it reaches a maximum and then drops again at high W/FM values when surface ablation reactions dominate. The maximum appears in the range W/FM = 5–10 × 10^8 J/kg for all isomers. When the plasma is turned on, pressure rises in the reactor with an amount, which also increases with W/FM. This pressure rise, ΔP, correlates with the refractive index increase, as indicated in Figure 2.

As pointed out by Yasuda,[15] the deposition rate of the plasma polymer is not a unique function of the energy input, as described by the composite parameter W/FM. They are also a function of the residence time in the plasma, as determined by the pressure, flow rate, and volume in the reactor. Hence, the normalized deposition rate, DR/FM, would be

a more "objective" quantity for comparison of deposition rates of the three DACH isomers, see Figure 1(b). For this quantity, the three DACH isomers follow the same curve at low W/FM values, but (especially) 1,3-DACH deviates at higher values. The reason behind this discrepancy is not yet clear but, as indicated below, plasma activated 1,3-DACH does show some distinct chemical features.

Figure 3 displays the *in situ* deposition rates obtained from QCM as a function of time after plasma ignition. The trend in deposition rate vs. W/FM is the same as in Figure 1. Notice that more than two minutes are required to reach steady state deposition rate. When W/FM was below the maximum value, the deposition rate generally decreased with time
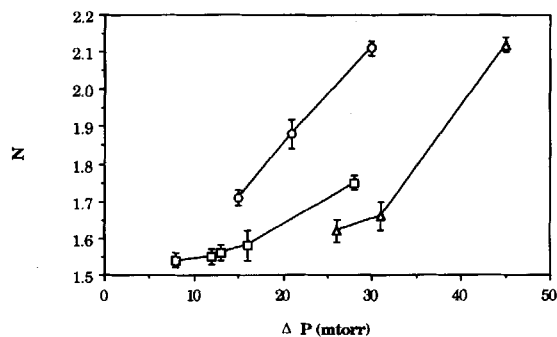
Figure 2 A plot of the refractive indices, N, of DACH plasma films, measured with ellipsometry, as a function of the immediate pressure rise, ΔP, occurring after plasma ignition. (□) 1,2-DACH; (○) 1,3-DACH; (△) 1,4-DACH.

1,2 DACH
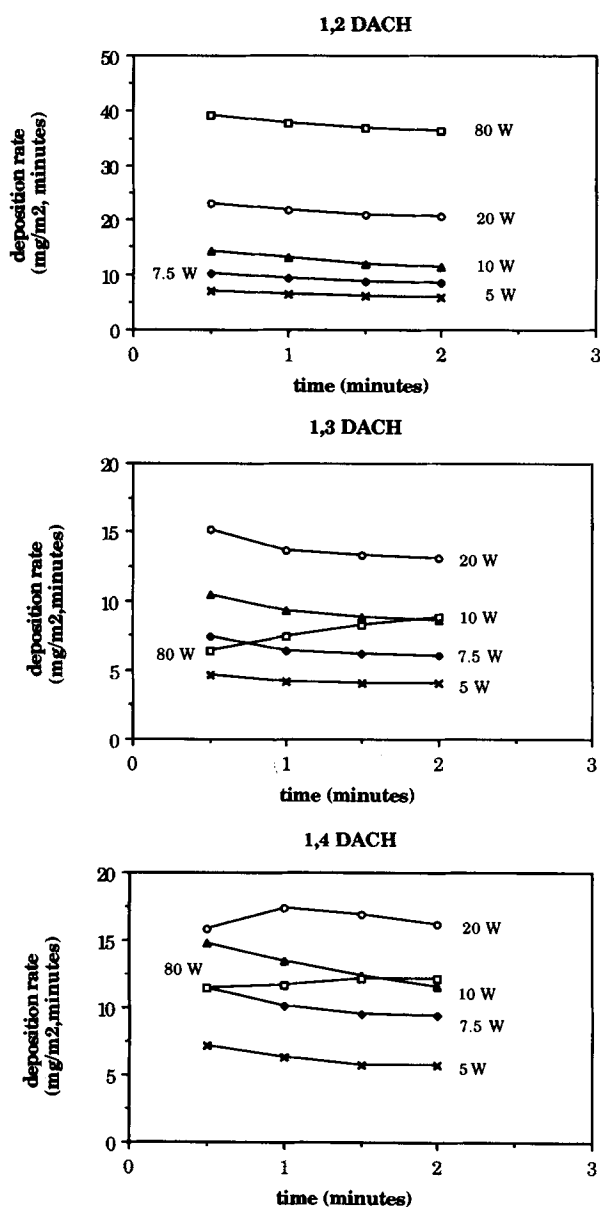
1,3 DACH

1,4 DACH

Figure 3 Deposition rates for the three DACH plasmas, measured by QCM, as a function of time after switching on the plasma; (X) 5 Watt; (◊) 7.5 Watts; (△) 10 Watts; (○) 20 Watts; (□) 80 Watts; (a) 1,2-DACH; (b) 1,3-DACH; (c) 1,4-DACH. Error bars have been left out for clarity. Typically the error was less than 5% of the mean value.

towards the steady state. On the other hand, when W/FM was above the maximum value, the deposition rate increased after plasma ignition towards a steady state value. The same trend (increasing or decreasing) towards steady state was also observed for the pressure following the initial pressure spike after plasma ignition. Hence, the deposition rate seems to correlate with pressure.

The average deposition rate for a single 1,2-DACH film (W = 7.5 Watts, W/FM = 3.4 × 10^7 J/kg), was also calculated from ESCA data. The number densities obtained were 25.4 ± 0.8 × 10^{15} carbon atoms and 3.6 ± 0.3 × 10^{15} nitrogen atoms per cm^2 per minute, which correspond roughly to 2.7 mg/m^2 per minute (24 Å/min). This value is in perfect agreement with that obtained by ellipsometry on SiO$_2$ (Table I).

Film Characterization

Before extensive characterization of the DACH films were performed, the stability upon storage in air was investigated by means of both ESCA and ATR-FTIR. It is obvious from Figure 4 that extensive oxidation of the films occurred within the ESCA sampling depth and a steady state composition is reached after approximately 15 days. When the plasma polymer is exposed to atmosphere, residual polymer radicals formed from labile hydrogens evidently caused oxidation of the film. This postoxidation surface is characterized by a fast phase, of large magnitude, occurring immediately upon atmosphere contact, and a slower phase, of smaller magnitude, also proceeding into the bulk of the film (at least > 10^3 Å), since oxidation products show up clearly in FTIR spectra for films on an ATR-cell of germanium (see Fig. 5).

The NH$_2$ doublet from liquid 1,2-DACH, appearing at 3356 and 3285 cm^{-1}, is, for the 1,2-DACH plasma polymer film, replaced by a broad peak, indicating both C — OH and NH functionalities. The narrow peak at 1596 cm^{-1}, also indicative of NH$_2$, also decreases and is replaced by several peaks in the range of 1580–1670, especially one at 1666, characteristic of C═O species and possibly NHC═O, which increases in magnitude over time. However, the CH$_2$ and CH signals from the DACH monomer at 2962, 2855, 1450, and 1387 cm^{-1} are still present in the plasma polymers. The carbon 1s ESCA signals for DACH films on SiO$_2$, deposited at W = 10 Watts, were deconvoluted into four peaks, corresponding to C — C, C — N, and C — O, C═O, C(═O)OH of the peaks on a desk computer. The result is displayed in Table II. The table indicates that the films contain various oxidized carbon species in addition to the C — N moiety. As a result of the above study of the time course of postoxidation reactions, all subsequent analyses were performed on DACH plasma films after storage for 24 days in air.

The surface composition of 1,2-DACH films (deposited at W = 7.5 Watts), deduced from ESCA
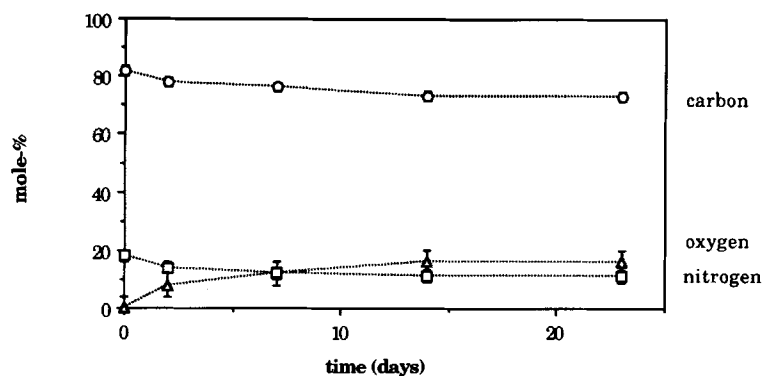
Figure 4   The progress of postoxidation reactions on 1,2-DACH plasma films deposited on LDPE, as made evident by the change in composition, measured by ESCA, after exposure to atmosphere up to 24 days; (O) carbon; (□) nitrogen; (△) oxygen.

data, was almost identical on polyethylene, mica, and SiO_2, except for a slightly higher degree of oxidation taking place for films on polyethylene (Table III). This is possibly due to hydrogen abstraction reactions on the substrate polymer, which result in more entrapped polymer radicals that will react with oxygen upon exposure to atmosphere. The composition on SiO_2 did not change with film thickness, but on PE, the oxygen content decreased continuously up to 500 Å, and then became identical to that of SiO_2 (unpublished data).

The effect of plasma energy input on the surface composition of DACH films on SiO_2, as obtained from ESCA analysis, is shown in Figure 6. Below 10 Watts, carbon decreases and nitrogen and oxygen increase with power for 1,2-DACH, indicating that postoxidation of the surface is reduced when using low energy plasmas. Above $W = 10$ Watts, no change in composition with energy input was observed for any of the DACH films and the composition of all three isomeric DACH films are similar, with approximately 77–79% C, 11–14% N, and 10–16% O.

This is also reflected in the invariability in contact angle data with varying W/FM (Fig. 7). At high power levels, the contact angle, ϕ, for the various DACH films did not change significantly with power and was slightly higher for 1,2-DACH films ($\phi = 58 \pm 3°$), as compared to 1,3- and 1,4-DACH films (both approximately $\phi = 50 \pm 3°$). The contact angle was identical for films on mica, SiO_2, and PE (except at low power levels with 1,2-DACH, e.g., thin films with $d < 50$ Å, on which the contact angle approached the value of pure PE, $\phi = 90°$, pure mica, $\phi = 7°$, and pure SiO_2, $\phi = 10°$, respectively).

The -NH_2 grafting yield for the three DACH films, as obtained from the ESCA F/N atomic ratio after PFB derivatization, decreases with W/FM (see

Fig. 8), which is most likely due to increasing secondary fragmentation reactions that are occurring in the plasma. We also noticed that the grafting yield decreases with film thickness. As an example, for a 1,2-DACH film produced at $W = 7.5$ Watts, the yield decreases from $11 \pm 1\%$ at $d < 50$ Å to $9 \pm 1\%$ at $d = 300$ Å, and $5 \pm 1\%$ at $d = 600$ Å. Nevertheless, these figures are surprisingly high and indicate that swelling of the film occurs during the PFB derivatization. Grafting yields were also determined ellipsometrically from thickness changes occurring as a consequence of the PFB reaction. As displayed in Table IV, there is excellent agreement between amounts determined from ESCA and ellipsometry.

The result from the elementary analysis of 1,2-, 1,3-, and 1,4-DACH plasma films, deposited at 20 Watts for 120 min, is shown in Table V. The elementary composition was similar for all three DACH isomers, except for the slightly different hydrogen content. All plasma films contained approximately 50% less nitrogen and approximately 40–60% less hydrogen, as compared to the pure DACH monomer, which indicates that one nitrogen and a number of hydrogen atoms in the DACH monomer were lost through the fragmentation reactions occurring in the plasma. Since there is an inverse relationship between hydrogen content and crosslinking density in the film, the data in Table V indicates that the 1,3-DACH film is somewhat more crosslinked, as compared to 1,2- and 1,4-DACH, which is supported by the refractive index and density data in Table I.

The mean molecular weight of the extracted polymers obtained from SEC analysis of ethanol supernatants was low, around $M = 500$ D. This indicates that a fraction of the plasma film does not attach chemically to the surface, but rather deposits as a homopolymer.
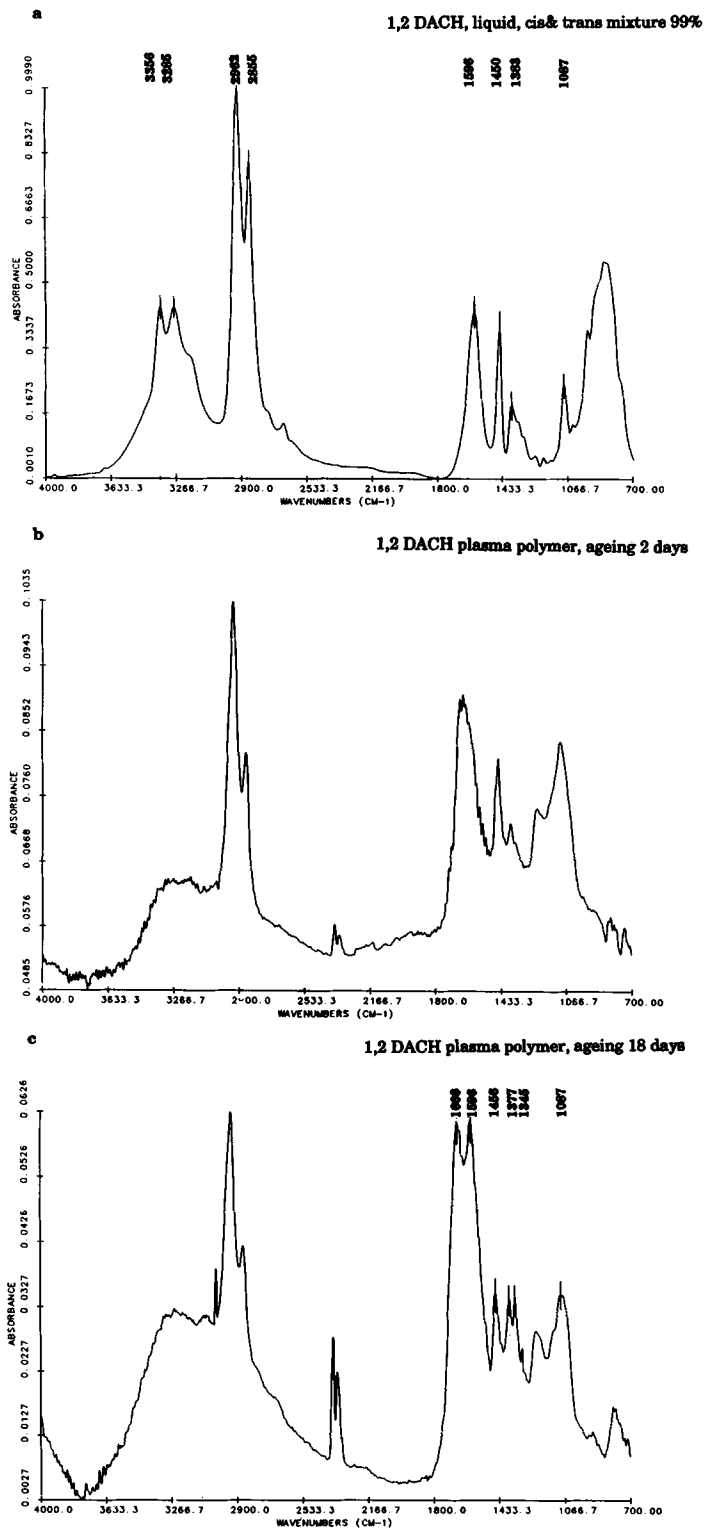
Figure 5   FTIR spectra of 1,2-DACH (a) liquid monomer, a mixture of cis and trans forms, 99%, from Aldrich; (b) 1,2-DACH plasma polymer (PP) film, deposited at 20 Watts, 5 min, on a Germanium ATR cell, and stored for 2 days; (c) 1,2-DACH PP film stored for 18 days.

Table II Relative Intensities Obtained from Deconvolution of Carbon 1s ESCA Signal of DACH Films Deposited at $W = 10$ Watts[a]

Sample	$C-C$ ($\delta E = 0$)	$C-N^b$ ($\Delta E = 1.0$)	$C=O$ ($\Delta E = 3.0$)	COO ($\Delta E = 4.2$)
1,2-DACH	1	0.19	0.16	0.07
1,3-DACH	1	0.33	0.18	0.05
1,4-DACH	1	0.22	0.14	0.06

[a] ΔE is the shift in the electron binding energy (in eV) relative to that for $C-C$ bond.
[b] Plus contributions from $C-O$ species.

Surface Force and Adhesion Measurements

The results from measurements with SFA on 1,2-DACH films, made at various power levels, are summarized in Table VI. The values for the refractive indices, obtained from ellipsometry (Table I), correlate well with those measured interferometrically for compressed films deposited on mica (Table VI), ($W = 7.5$ Watts, $N = 1.55$; $W = 80$ Watts, $N = 1.75$).

The thickness determined by this technique, however, is much greater (e.g., at $W = 20$ Watts) than that determined by ESCA on mica or by ellipsometry on SiO_2. This discrepancy may be due to two factors. The first is that surface asperities (as indicated in Fig. 9 for swelled film) or minor film roughness will result in slightly larger thickness values with the SF Technique. The second reason is that the films prepared for SF measurements were not rinsed with ethanol (which removes homopolymers) before measuring, as this may lead to irreproducibility in the distance and adhesion results.

Also, the increase in thickness with plasma power tended to be of larger magnitude on mica. In contact in the SFA, the films are under the pressure of the adhesive force. At low plasma powers, it could be seen that, as the separating force was increased, the film thickness increased slightly, that is, the films "decompressed" by a few Ångströms per surface, corresponding to 5–10% of the total film thickness. This decompression is most likely due to the little

Table III ESCA Characterization of 1,2-DACH Films Deposited on Various Substrates at $W = 10$ Watts ($W/FM = 4.5 \times 10^7$ J/kg)

Substrate	C (mol %)	N (mol %)	O (mol %)
Polyethylene	76	12	12
SiO_2	79	13	8
Mica	79	12	9

crosslinking obtained in films produced at these powers. Thus, when the compressive load of the mutual attraction of the surfaces is removed, the polymer strands tend to expand due to the entropic effects. The higher adhesion force observed for the lowest power is probably due to the emeshing of chains between the two surfaces.

At high powers, the film appeared more rigid and no decompression was observed upon reduction of the load. The adhesion forces yielded values that were typical of medium-energy (polar) polymer surfaces and did not change above the lowest power of 7.5 Watts.

The surfaces in contact flatten, due to the deformation of the glue on which the mica sheets were mounted, and typically the area sampled at each contact was about 0.001 mm^2. Over such flattened areas, the thickness appeared uniform (to within about 2 Å). However, the adhesive force tended to flatten surface asperities, since they experience a greater pressure.

Scanning electron micrographs of water vapor-exposed films [see Fig. 9(b)] indicate that any asperities are of submicron size. The thickness varied somewhat from contact to contact for films deposited at low power (of the order of 20%), but for films deposited at high power ($W = 60$ and $W = 80$ Watts), the compressed thickness varied by only a few Å. This seems to be a remarkable feature of a film that is hundreds of Ångström thick. As there is no observable decompression prior to the jump apart, it seems reasonable to assume that the measured value is close to the "true" thickness of the film. It seems likely that this smoothness must be imposed by the substrate. However, the polymerization rate must also be even for such uniformity to be propagated over hundreds of Ångströms.

When the plasma polymer surfaces were exposed to water vapor, the films were observed to "swell." The swelling, or possibly buckling of the film due to internal stresses, was difficult to quantify, since the film became easily damaged when wet and, for films
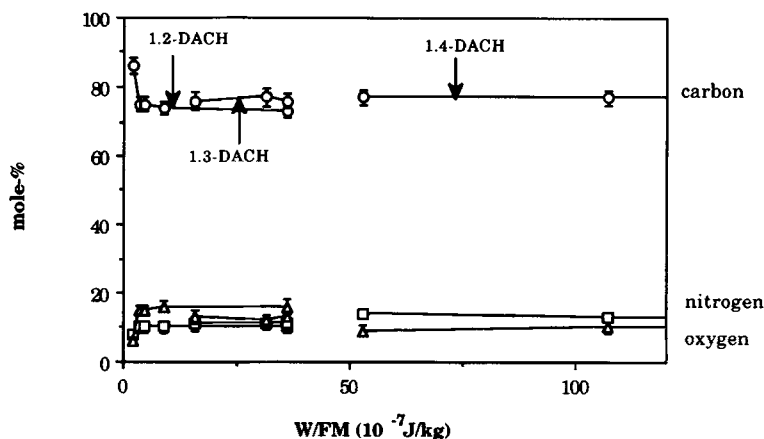
Figure 6 The composition, in mol %, of various DACH-isomer plasma films, 5 min deposition time, measured by means of ESCA as a function of W/FM, 24 days after deposition; (O) carbon; (□) nitrogen; (△) oxygen.

deposited at a power higher than $W = 40$ Watts, the damage usually rendered measurements of the swelling impossible. When measurable, the swelling was 30–50 Å per film and appeared to be independent of power (and film thickness, see Table VI). The pull-off force between the surfaces increased in water vapor and the capillary condensate usually appeared when the surfaces were brought into contact. When measurable, the refractive index decreased slightly, indicating the inclusion of material with lower refractive index [$N(H_2O) = 1.33$]. The film expanded and, after separation, the surfaces were damaged. Presumably, the surface was rendered susceptible to damage, due to softening of the film by weakening hydrogen bonds, or by the dissolution of a nonsur-

face-grafted homopolymer in the capillary condensate.

The most interesting effect of swelling was that observed at the highest power [$W = 80$ Watts, see Fig. 9(a) and (b)]; surface force measurements are no longer possible (due to surface roughness), but, under an optical microscope and SEM, a pattern became discernable on the disc. The pattern appeared to consist of 2-ply ropes of some extruded material, which formed extremely regular, macroscopic formations on the surface. Typically, the repeat distance and the amplitude of the sinusoidal formation were of the order of 60 μm and 30 μm, respectively. Although there was variation between different strands in the period and amplitude, the variation in these two parameters within a particular strand was negligible.
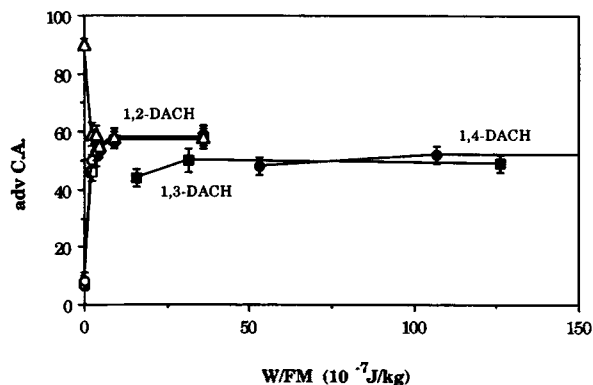
Figure 7 Advancing contact angles (Adv CA), as a function of W/FM for the three DACH-isomer plasma films deposited on SiO_2, mica, and polyethylene. Deposition time was 2 min. (□) 1,2-DACH on mica; (O) 1,2-DACH on SiO_2; (△) 1,2-DACH on PE; (■) 1,3-DACH on SiO_2; (●) 1,4-DACH on SiO_2.
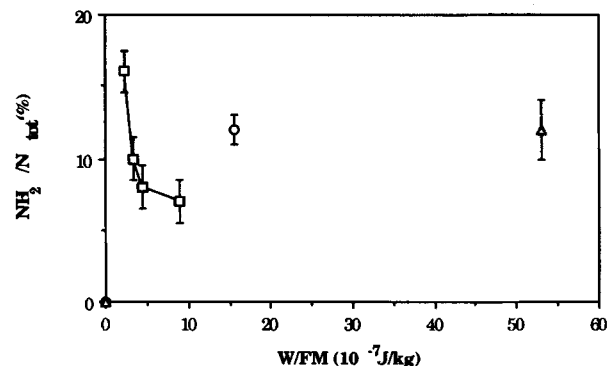
Figure 8 The influence of W/FM in various DACH plasmas on the density of NH_2 groups, accessible to reaction with pentafluoro benzaldehyde, as quantified by the Fluorine to Nitrogen ratio in ESCA. (□) 1,2-DACH; (O) 1,3-DACH; (△) 1,4-DACH.

Table IV   Grafting Yield (NH₂ Groups Reacting with PFB in Atom % of the Total N Content) on 60 Å Thick 1,2-DACH Films Deposited on SiO₂ at Various Power Densities[a]

W/FM $(\times 10^{-7}$ J/kg)	$F/5N$ (mol %) (ESCA)	PFB/N (mol %) (Ellipsometry)
0	0	0
2.3	16 ± 2	21 ± 5
3.4	10 ± 2	11 ± 4
4.5	8 ± 2	8 ± 3
9.0	7 ± 1	4 ± 3
36.0	0 ± 1	0 ± 2

[a] A comparison between ESCA measurements and ellipsometry: In the ESCA measurements, 1 mole PFB corresponds to $\frac{1}{5}$ of the fluorine intensity. Constants used in ellipsometry: $M/A_{PFB} = 3.8563$, $M/A_{DACH} = 3.43$.

It is likely that the regular pattern is a way to minimize the free energy of the film, but the basic reason behind this phenomenon is unknown. The origin must, however, be related to the swelling of the film and the resulting strain imposed on the rigid crosslinked structure of the polymer. It is difficult to ascertain whether the formations are associated with cracking of the surface or whether matter is forced into the surface to relieve a pressure increase within the film on swelling. It should also be considered a possibility that the swelling of the film is due to the insertion of a water film between the mica and the polymer film. It is not possible to distinguish between these two possibilities using the surface force technique.

Finally, the adhesive properties of 1,2-DACH plasma films were measured in a technical laminate between polyethylene and polyamide films. The T-peel test resulted in an increase in adhesion from zero to 80 ± 5 N/m, when the 1,2-DACH film was deposited on PE, at low energy input, $W = 7.5$ Watts. The most reasonable explanation for this adhesion is H-bonding between various polar groups, observed on the DACH surface and the amide groups on poly-

amide, as well as the transamidation reactions that may occur at the elevated temperature that was used during lamination.

Tentative Plasma Polymerization Mechanism

C-N Cleavage

Based on the similar composition obtained for all three DACH isomers (C/N ratio is approximately 6), we postulate that the plasma polymerization and deposition mechanism is similar for all three isomers and starts with the release of an NH₂ radical and the creation of an aminylradical (AR) radical. This is because the C-N cleavage reaction requires the lowest energy. The NH₂ release, which leads to a sudden pressure increase, most likely occurs above a minimum value in energy input. This value is low for DACH, since release is observed even at the lowest energy input on 1,2-DACH. The reactions for 1,3-DACH are shown in Figure 10 (species 1). The AR-radical is central for the polymerization for all three isomers. It may easily undergo transition in various ways, as indicated in Figure 10. The energetically most favored subsequent route after cleavage would be ring-opening to form allylic radicals, which can polymerize and form a crosslinked film. Similar cleavage reactions occur for 1,2- and 1,4-DACH. However, the ring opening reaction is particularly favorable for 1,3-DACH, which could generate a species with a resonance stabilized double bond (species 2).

C1-C2 Cleavage

Hypothetically, 1,2-DACH could form a polymer by C1-C2 cleavage, resulting in the formation of biradicals, which instantaneously can polymerize, but the surface composition ($N/C \approx 1/6$) indicates that this cleavage has a lower probability, which also follows from rough free energy considerations. These considerations also hold for 1,4-DACH. However, release of aminylradicals and resonance stabilization

Table V   Chemical Composition of Diaminocyclohexane (DACH)-Plasma Films Deposited at $W = 20$ Watts, as Determined from Elementary Analysis[a]

Sample	C (w/w %)	H (w/w %)	N (w/w %)	O (w/w %)	Deduced Formula
1,2-DACH	75.1 ± 5.9	8.5 ± 1.4	15.6 ± 1.5	0.8 ± 0.3	C_6H_8N
1,3-DACH	78.8 ± 6.5	5.5 ± 1.3	15.0 ± 1.0	1.2 ± 0.2	C_6H_5N
1,4-DACH	77.2 ± 2.5	6.6 ± 1.2	15.5 ± 0.9	0.7 ± 0.2	C_6H_6N

[a] Notice that the energy input was different for the three DACH isomers, due to different flow rates (see Table I).
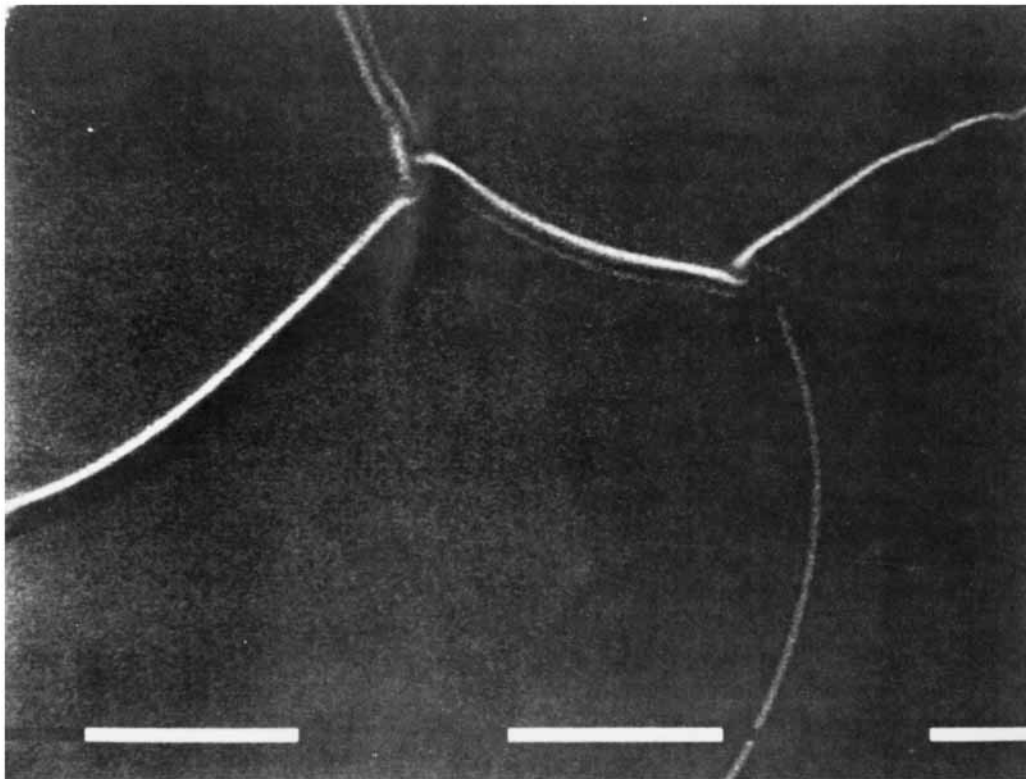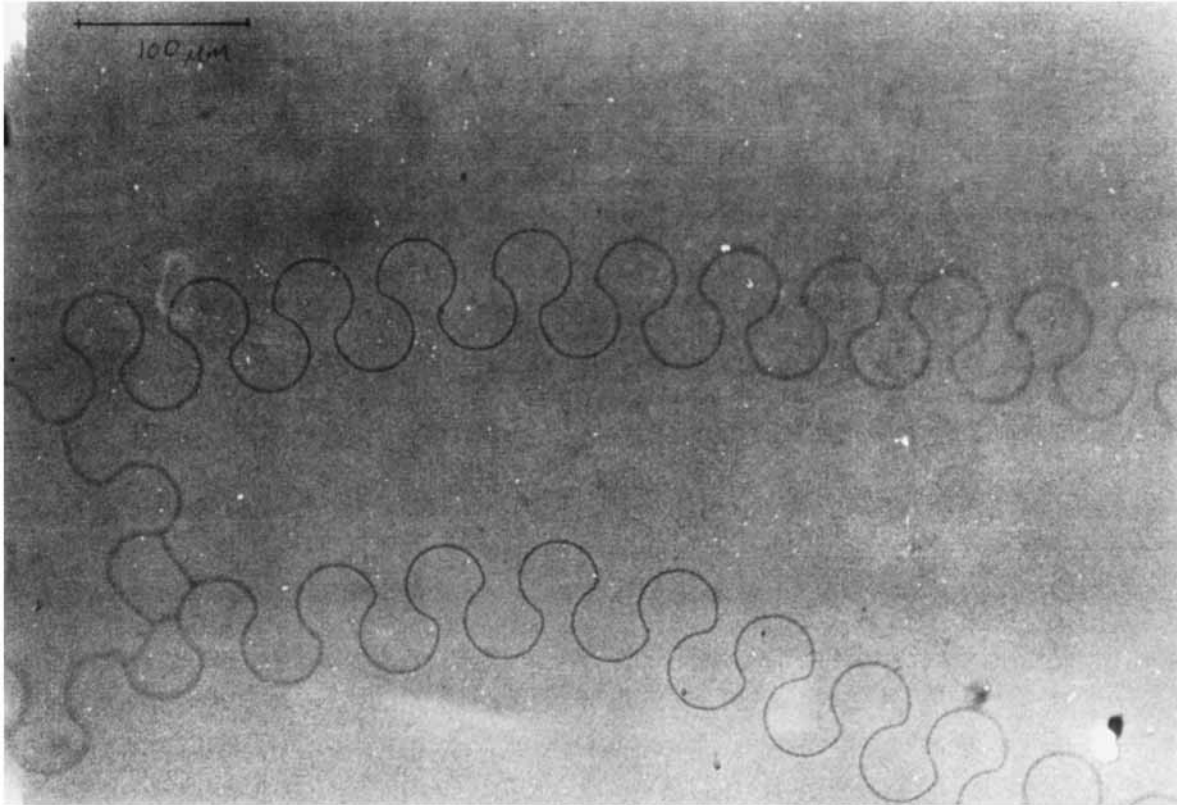
Figure 9 Scanning Electron Micrograph of a 1,2-DACH film deposited at 80 Watt (3 min) after exposure to water vapor; (a) 100 μm grid, (b) 10 μm grid.

Table VI Result of the Measurement With a Surface Force Apparatus on Dry 1,2-DACH Films[a]

| W/FM (10^{-7} J/kg)	Refractive Index N_f	Average Film Thickness, d (Å)	Surface Energy, ($F =/3\Pi R$ (mN/m))
3.4[b]	1.55 ± 0.05 (1.4)	60 ± 10 (87)	25 ± 2 (37)
3.4[c]		63 ± 6 (80)	44 ± 8 (72)
3.4[d]		34 ± 4 (75)	60 ± 12 (89)
9.0	1.63 ± 0.01 (1.61)	388 ± 4 (430)	20 ± 1 (43)
18.0	1.67 ± 0.01 (1.64)	435 ± 5 (465)	18 ± 4 (18)
27.0	1.65 ± 0.01	465 ± 4	29 ± 1
36.0[b]	1.75 ± 0.01	485 ± 4	16 ± 5
80[c]		673 ± 8	26 ± 3

[a] Deposition time t = 3 min. Data within brackets refer to wet films.
[b,c,d] Different sample preparations. The film thickness is the average thickness of several contact positions between the same surfaces.

is possible for 1,3-DACH, which may again result in a polymer with an atomic N/C ratio of $N/C \approx 1/6$, as observed experimentally. Other cleavages are even less probable, except for the C1–C6 cleavage

for 1,3-DACH. It is reasonable to believe that the unique resonance stabilization mechanisms, present for 1,3-DACH as described above, is the ultimate reason for the higher crosslinking density and re-
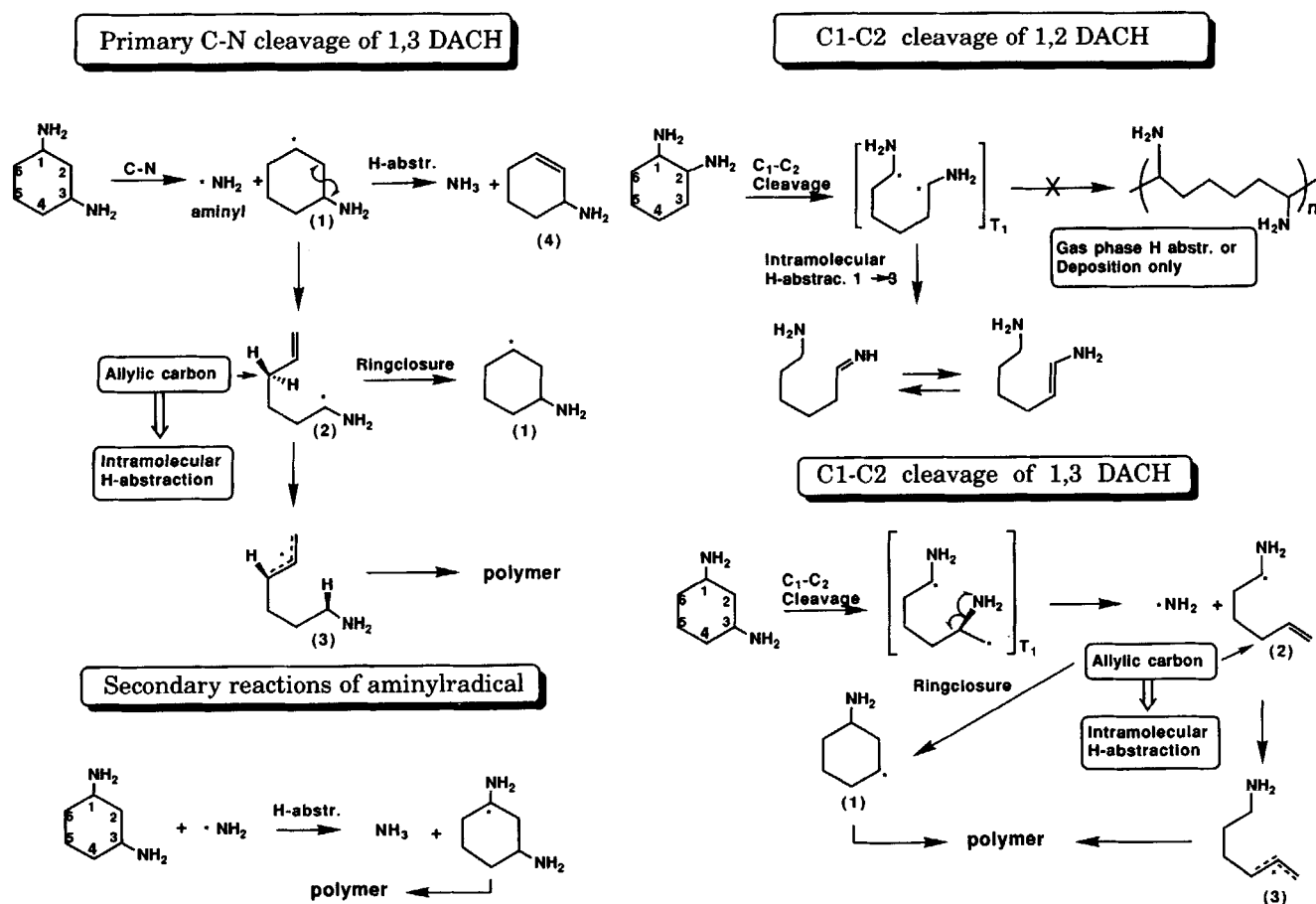
Figure 10 Some possible fragmentation and polymerization reactions occurring in DACH plasmas: (a) the C–N cleavage reaction for 1,3-DACH, (b) C1–C2 cleavage reactions for 1,2-DACH and 1,3-DACH. For details see text.

fractive index of this film [and maybe also for the lower (maximum) value, above which ablation reactions start to dominate].

The pressure change with time after plasma ignition can tentatively be explained in the following way: When AR-radicals react with virgin DACH molecules entering the chamber, less active products are formed, pressure drops (NH_3 is pumped out), and the deposition rate decreases. In contrast, above the maximum value, extensive fragmentation initially occurs, leading to low molecular weight active species and, hence, lower mass deposition rate. These LMW products are also easily pumped out of the chamber. As they start to abstract hydrogens, or react with virgin DACH monomers, AR-type radicals can form again, which leads to an increasing polymerization rate with time after ignition.

CONCLUSIONS

When depositing any of the three isomers of DACH from an RF plasma, an aminylradical is cleaved off and the N/C atomic ratio of the plasma polymer formed (part of which is an extractable homopolymer) is $\approx 1/6$. The plasma polymer proceeds to oxidize up to several weeks upon exposure to atmosphere and hydroxyl and carbonyl groups appear also deep inside the film. However, as much as 10–15% of the total nitrogen content still reacts as intact NH_2 groups at low plasma energy input ($10^7 \, J/kg$). The water contact angle is approximately 55° and the film is soft and swells in water. The film densities obtained during these conditions are slightly above 1 g/cm³, the refractive indices around 1.5, and the deposition rate is around 20 Å per minute. When the energy input increases, the deposition rates generally increase to a maximum of around 50 Å per minute, and then they decrease again, while the film densities and the refractive indices continuously increase to above $N = 2$ and $\delta = 2$ g/cm³, and the films become hard. The behavior of all three isomers

are similar, with a minor difference for 1,3-DACH, possibly due to differences in resonance stabilization of the various aminylradicals formed in the plasma. For 1,2-DACH films, (the only film studied in this respect), when produced at high energy, internal stress results in formation of an extremely regular pattern of extruded material on the surface.

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