Mechanical Failure in Thin-Film Nonlinear Optical Polymers: Structure and Processing Issues

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SYNOPSIS

Stress developed during the spin-coating process often initiates cracks leading to failure in nonlinear optical devices. The primary intrinsic reasons for this were shown to be a lack of a secondary relaxation process below the glass transition as well as an insufficiently large molecular weight to enhance toughness by chain entanglement, as detected by dielectric measurements and viscoelastic shear moduli, respectively. A detailed systematic synthetic effort was undertaken to increase the chain length through improved free-radical methods. Results showed that as the molecular weight was raised chain entanglements were observed and film toughness was improved as evidenced by the thicker, crack-free film attained. As well as thermal stresses, solvent stress cracking was identified as a major source of fabrication defects in the multilayer spin-coating process. A plasma polymer layer deposited on the film surface was successful as a barrier layer preventing solvent penetration and crack formation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

For thin polymeric film waveguide applications, the fabrication process necessitates a solution casting by the spin-coating process, followed by a thermal drying step. As a result of this, defects or cracks often initiate, due to stress development, causing device failure. To improve device efficiency, cracking causes were elucidated, then investigated. Intrinsically, a polymer will fail if it has insufficient mechanical strength on application of a stress load or has low impact resistance. The brittleness is believed to result, in the case of side-chain nonlinear optical (NLO) polymers, from the inability to absorb impact energy through sub glass transition relaxation mechanisms.[1] This is due to suppression of chain mobility and increased stiffness caused by the highly polar side-chain groups, allowing little plastic deformation.

During the processing drying stage, the associated volume decrease causes stress development, especially at any defect points. To prevent failure, the material must have sufficient toughness to tolerate these high-stress concentrations. Polymer toughness is significantly enhanced by interchain entanglements that can form only if an entanglement molecular weight is achieved. In the case of polymer molecules whose molecular weight is large enough to form entanglements, fracture occurs in two stages.[2-4] The first involves the orientation and elongation of polymer chain segments between entanglement points until the entanglements experience stress and begin to dissolve. In the second stage, the fracture occurs at the critical stress through either mechanisms of chain pullout or chain scission depending on the time scale of the local fracture event. It has been suggested that the viscous energy necessary to overcome the frictional drag of the entanglements during the first stage of the fracture is the major contributing factor to the overall toughness of glassy polymers. These entanglement points normally exist in a knotlike form with a folded back structure. It has been documented[5] that comb-shaped backbone polymers suppress this conformation and require longer main-chain lengths to allow stable entanglements. The interference between the bulky side groups limits the variety of conformations, and, thus, rather loosened three-dimensional networks may be constructed.

The effect that secondary relaxation processes

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have on polymer ductility below the glass transition was examined through thin-film dielectric and mechanical properties. Polymer viscoelastic behavior was used to probe the degree of entanglement by surveys of the complex modulus over a range of frequencies. These data were used to show that only high molecular weight samples had evidence of necessary molecular chain entanglement and that these were less brittle than were low molecular weight samples.

To improve both tensile strength and toughness, efforts were made to investigate the influence that both process-related variables and intrinsic structure properties have on film mechanical properties. First, the molecular weight of the polymer was increased through both improved synthesis and cross-linking, and the effect of resultant increases in both melt viscosity and modulus was evaluated with regard to the thickest crack-free films achievable. Process-related issues were also examined, such as reduction of thermal stress development by evaluating alternate substrates, solvents, and temperature effects as well as by eliminating solvent stresses by plasma techniques. Each of the above is examined and discussed.

POLYMER VISCOELASTICITY

Examination of the viscous flow under shear stress and quantitative analysis of both the loss and storage moduli as a function of rate of shear can give detailed information about chain lengths and interactions. Investigation into the polymer rheology is possible by experimental determination of the melt viscosity and shear modulus as a function of both shear rate and temperature. The bulk viscosity (η) is related to the polymer chain length (Z) by the following equations,[6] where K_1 and K_2 are temperature-dependent constants:

$$\log \eta = 3.4 \log Z + \log K_2 \qquad (1)$$

$$\log \eta = \log Z + \log K_1 \qquad (2)$$

Equation (1) is valid above a critical chain length Z_c where entanglement of the polymer chains can occur. A measure of this entanglement can also be experimentally determined on examination of the viscoelastic behavior of the loss (G'') and storage (G') shear moduli as a function of shear rate. As entanglement becomes more significant, at low shear rates, the elastic or storage modulus curve exhibits a more plateaulike region, as flow is retarded and

becomes larger than the value of G''.[7] For the polymer series synthesized, which is an aminonitrostilbene methacrylate copolymer (P2ANS/MMA), at low molecular weight, the value of G'' is always higher and G' does not exhibit plateaulike behavior. This is best illustrated by Figure 1, which shows examples of both high and low molecular weight NLO polymers A and B. As is clearly seen, the higher molecular weight polymer A shows that the G' curve not only intersects the G'' curve, but also that it has far less variation with shear rate than the low molecular weight sample B. This indicates that some kind of interchain entanglement exists for this polymer. Film evaluation of all polymers that exhibit this characteristic show higher stress tolerance and improved toughness that manifests as fewer cracks. This technique was therefore useful to evaluate the polymers in terms of their effective entanglement and toughness.

THE EFFECT OF CHROMOPHORE CONCENTRATION ON THE DIELECTRIC AND MECHANICAL PROPERTIES OF AN NLO COPOLYMER

Besides the influence of chain entanglement, another significant structural factor that affects toughness of polymers is the presence of a secondary relaxation process below the glass transition temperature. Ductile glassy polymers have pronounced low-temperature secondary relaxation processes that can be observed in their dynamic electric thermoanalysis spectra. The motions of short sections of side chains are believed to be related to ductility and toughness of polymers in that they afford an energy-release mechanism.

The generalized dielectric constant of a material can be found by the complex quantity ε^*:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad (3)$$

where $i = \sqrt{-1}$. The real component, ε', is equivalent to the dielectric constant, and the imaginary component, ε'', is the loss factor. Another commonly used term for expressing dielectric response is the dissipation factor, or loss tangent:

$$\tan \delta = \varepsilon''/\varepsilon' \qquad (4)$$

Composition ratios of 5/95, 10/90, 25/75, 35/75, and 50/50 of a side-chain NLO chromophore methacrylate copolymer (P2ANS/MMA) as well as the pure PMMA were used to study the effect of

(a)

(b)
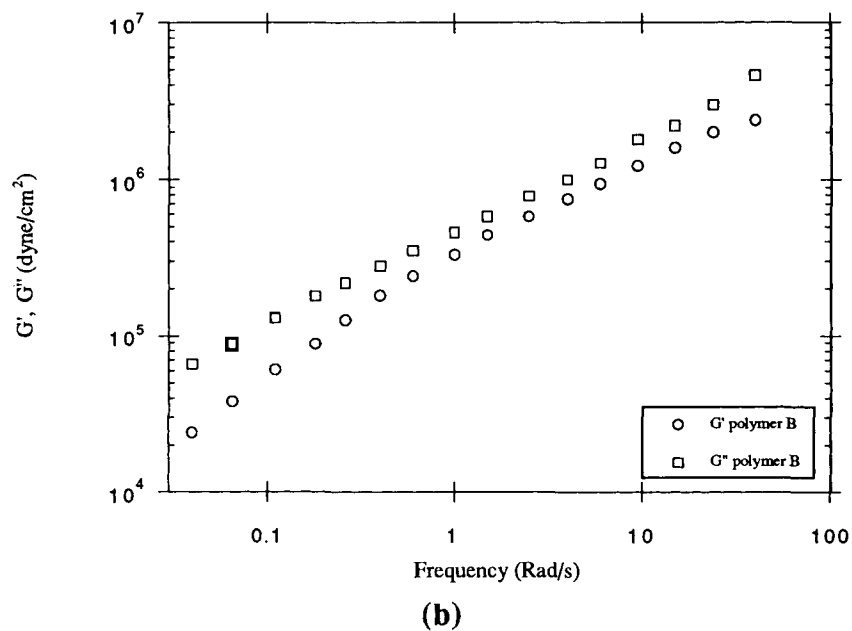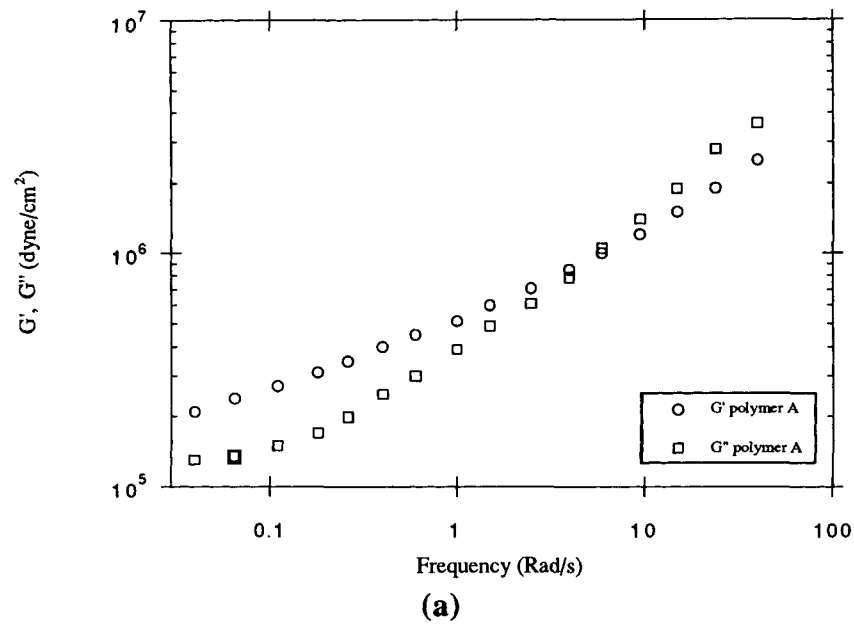
Figure 1 Storage (G') and loss (G'') moduli as a function of frequency for (a) high molecular weight polymer and (b) low molecular weight polymer.

dipolar interaction on polymer ductility. Their dielectric properties were measured as a function of temperature from −50°C to above their respective glass transition (T_g) at a rate of 1°C/min using a Polymer Laboratories dielectric thermal analyzer. The samples were of the form of a thin film of a few microns thick spun on silicon substrates. A gold electrode was thermally evaporated onto the film as one of the electrodes and the silicon substrate served

as the other electrode for the dielectric measurement. The data were taken at 20 Hz.

Figures 2 and 3 show, respectively, the real and imaginary parts of the dielectric constant. It can be seen that ε' of all the samples follows a similar trend and rises sharply at the T_g. At this temperature, ε' increases with NLO concentration from PMMA to the 50/50. This increase can be explained by the increasing dipole strength in the polymer arising
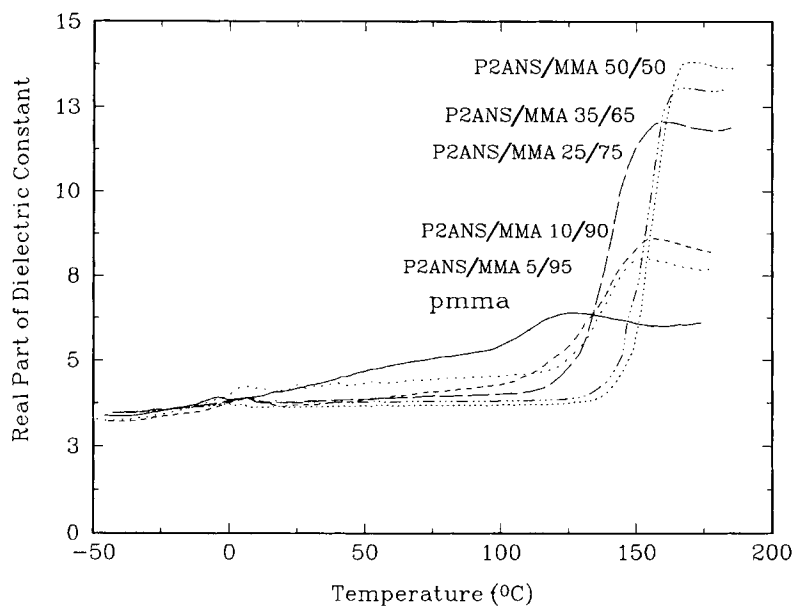
Figure 2   Effect of NLO composition on the dielectric constant of P2ANS/MMA copolymer.
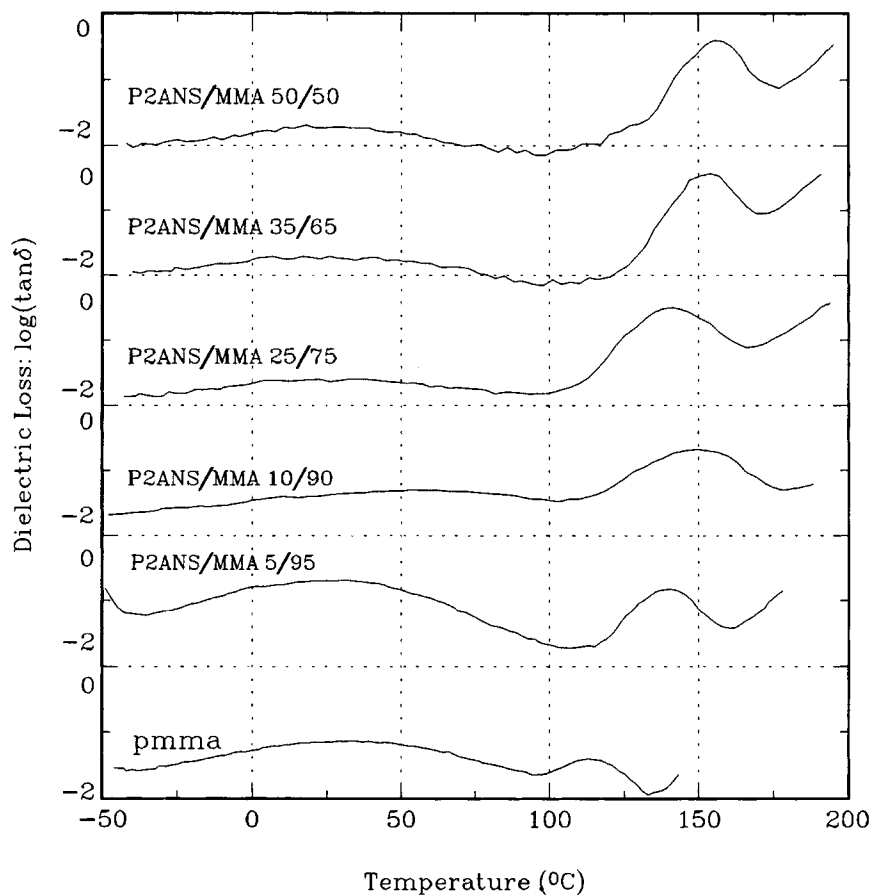
Figure 3   Effect of NLO composition on the dielectric loss of P2ANS/MMA copolymer.

from the relatively large dipole moment (approximately 7 Debyes) of the aminonitrostilbene NLO side chain. At T_g, these dipoles are free to move under the applied electrical field; hence, the increase in ε'. At ambient temperatures, however, ε' behaves in the opposite manner as it decreases with increasing NLO concentration, despite the increase in the number of dipoles. This behavior is explained by the increase in dipolar interactions that limits the mobility. It is well known that PMMA has a β relaxation peak at ambient temperatures associated with

the mobility of the carbonyl group. This peak is clearly seen in the dielectric loss spectrum of PMMA in Figure 3. As the concentration of the stilbene side chains increases, this β peak initially increases in magnitude but is quickly quenched by more than one order of magnitude in its loss tangent when it reaches the 50/50 ratio. This behavior can be explained by competition between the increasing number of dipoles that results in increased dielectric loss and dipolar interaction that limits the mobility of these dipoles. It is this β relaxation at ambient
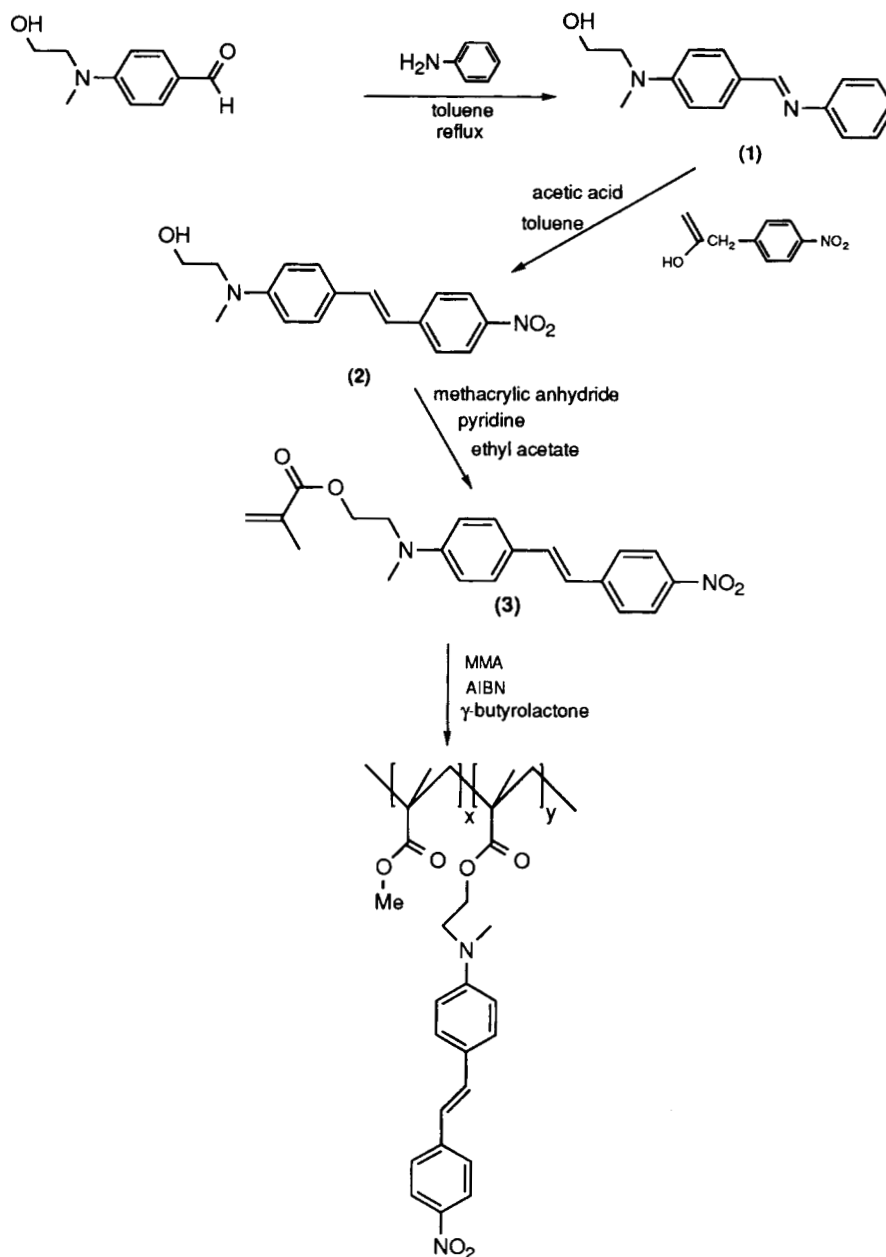
Scheme 1 Synthesis of P2ANS/MMA copolymer.

temperatures that plays an important role in the mechanical toughness of a polymer because it allows the polymer to flex instead of stress release through the formation of cracks.

In the present study, the mechanical strengths of the above series of copolymers were compared by spinning and drying increasingly thick films on silicon substrates until cracks appeared. The films were spun out of cyclohexanone solvent onto silicon substrates and dried in a 160°C oven for 6 h. The results confirmed that the thickest crack-free films could be formed from PMMA and the lowest chromophore volume ratio, and this thickness decreased with increasing NLO concentration. Thicknesses above 100 μm were successfully fabricated using this method with PMMA and the lowest chromophore volume ratio, whereas for a 50% molar incorporation of NLO side chain, this thickness was approximately 10–20 μm.

HIGH MOLECULAR WEIGHT POLYMERS

Polymerization Behavior

The polymerization synthetic scheme involves the free-radical polymerization of the aminonitrostilbene containing methacrylate as shown in Scheme 1.[8] The chemical nature of this monomer and, in particular, the redox potential of the aminonitrostilbene functional group, was expected to have radical propagation quenching ability. This makes the synthesis of a high polymer more difficult. Experimental parameters such as monomer and initiator

concentration, solvent, and temperature were systematically varied to investigate the effect on degree of polymerization and, hence, on the molecular weight. The molecular weight variations from sample to sample were probed by both melt and intrinsic viscosity. Direct comparisons were somewhat complicated by composition differences and molecular weight distribution variations.

Table I shows a polymer series' rheological and film behavior over a range of molecular weights. Empirically, as the molecular weight increased, thicker structures were able to be supported. This is evidence of the improved mechanical integrity of these samples. The polymers' molecular weight was varied by adjustment of the experimental parameters, which is examined in more detail in the following sections.

Dilute solution viscosity was used in this case as a measure of polymer molecular weight. As the hydrodynamic volume of the polymer coil is dependent on the solvent–polymer interactions, the relative coil size for a copolymer is a function of both molecular weight and composition distribution. The molecular weight of a polymer is related to the intrinsic viscosity by the Mark–Howink equation[9] where K and α are the Mark–Howink constants for a particular solvent and temperature:

$$[\eta] = KM^{\alpha} \qquad (5)$$

Polymerization Kinetics

It was assumed that both monomers have equal reactivity ratios and that the resultant copolymers

Table I Polymer Properties

Polymer Composition	Experimental Conditions $[M]/[I]/T$/Solvent	T_g (°C)	Melt Viscosity (10^5 Poise)	Intrinsic Viscosity (dL/g)	Cracking Thickness (μm)
50/50	10/0.2/75/DCE	146	0.75	0.13	12
50/50	10/0.1/75/DCE	146	0.71	0.14	15
50/50	15/0.1/65/DCE	148	0.85	0.19	> 10
50/50	15/0.2/60/DCE	145	0.89	0.19	> 7
50/50	20/0.1/70/DCE	144	0.6	0.20	14
50/50	20/0.1/70/DMSO	145	0.97	0.21	> 6
50/50	25/0.1/70/DCE	147	1.4	0.21	18
50/50	20/0.1/70/BLAC	144	1.5	0.28	20
50/50	30/0.1/70/DCE	142	1.6	0.31	> 18
50/50	25/0.1/80/BLAC	147	1.1	0.35	27
50/50	25/0.1/70/BLAC	143	2.3	0.35	23
50/50	30/0.1/80/BLAC	144	1.7	0.39	> 32
50/50	40/0.1/75/DCE	143	0.75	0.40	> 35
50/50	30/0.1/70/BLAC	144	2.2	0.46	> 30

have a statistically random composition distribution. This is supported by ^{1}H-NMR. Both monomers react with propagating radicals with almost identical enthalpies; however, their steric, solubility, and diffusion differences suggest that they would not be kinetically equivalent. The number-average degree of polymerization (X_n) can be defined as the polymerization rate (R_p) divided by the sum of all the termination and chain-transfer rates. This can be expressed by the Mayo equation[10]:

$$\frac{1}{X_n} = \frac{(1+\alpha)k_t R_p}{k_p^2[M]^2} + C_m + C_i\frac{[I]}{[M]} + C_s\frac{[S]}{[M]} \quad (6)$$

where $\alpha = 0$ or 1 dependent on whether termination is exclusively by combination or disproportionation, and $C_m = k_{tm}/k_p$, $C_i = k_{ti}/k_p$, and $C_s = k_{ts}/k_p$, where k_t is the appropriate rate constant for termination.

Effect of Monomer Concentration on Polymer Molecular Weight

The kinetic chain length (ν) is shown to be related to monomer concentration by eq. (7):

$$\nu = \frac{k_p[M]}{2(f k_d k_t[I])^{0.5}} \quad (7)$$

where k_p, k_d, and k_t are the rate constants of propagation, dissociation of initiator, and termination, respectively, and f is the initiator efficiency. A high monomer concentration will also reduce the effects of chain transfer to solvent[11] as the derivation for $1/X_n$ contains the term $C_s([S]/[M])$.

The results shown in Figure 4 indicate that the polymer molecular weight increases with increasing monomer concentration. However, at high concentrations, the final copolymer composition is not as sensitive to the stoichiometry of the feed mixture, resulting in some copolymer ratio discrepancies.

Effect of Solvent on Polymerization

In solution polymerization, the nature of the solvent plays an important role in the kinetics of both polymerization and termination. The solvent chain-transfer constant becomes significant when it has a labile atom such as chlorine that forms a stable radical, causing chlorinated solvents to have high chain-transfer constants.[12] Also, the effectiveness of the transfer reaction can be shown to be dependent on the electronic environment or polarity of the propagating radical and its interactions with solvent. If the resultant solvent radical has a low reactivity with the monomers, the polymerization rate is retarded.[13]
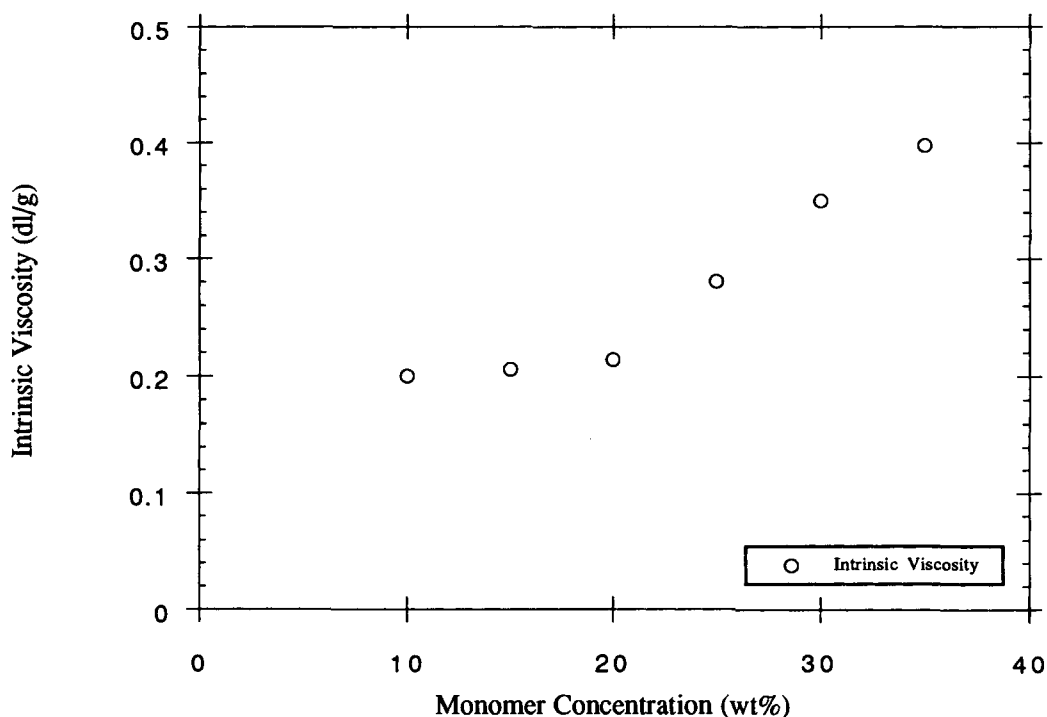
Figure 4 Effect of monomer concentration on polymer intrinsic viscosity.

If there is a resultant net inhibition, not only molecular weight but yield is also reduced.

The rate of chain termination is also sensitive to the solvent in that it is diffusion-controlled. This manifests in both translational and segmental diffusion. With increased conversion, both the solvent quality and radical coil size decreases. This has the effect of increasing segmental diffusion, enhancing the probability of reaction, and, hence, increasing the termination constant. However, at higher conversions, translational diffusion becomes dominant. The resultant increase in viscosity decreases both chain mobility and the probability of chain-end reactions. As monomer diffusion is still relatively unaffected, an autoacceleration[14,15] or gel effect can take place, resulting in a high degree of polymerization. The solvent quality influences the coil size and, hence, the concentration of polymer required to induce the onset of this effect. Three solvents were used for polymerization, namely, dichloroethane (DCE), γ-butyrolactone (BLAC), and dimethyl sulfoxide (DMSO), and the molecular weights obtained were compared.

The results indicated that chain transfer to solvent appeared to have a significant effect on the degree of polymerization. As the chain-transfer constant of the solvent increased, the degree of polymerization decreased. The occurrence or influence of solvent on the gel effect was not investigated, although it was believed that the solution viscosity did not increase to necessary levels. The degree of polymerization was highest in butyrolactone where the yield was a little better, chain-transfer effects were minimal, viscosity was higher, and the buildup of high polymer was possible.

Temperature Effects on Polymer Molecular Weight

Analysis of the optimum temperature for polymerization was complicated due to various competing effects of kinetics, thermodynamics, and solution behavior. The rate-determining step in the polymerization process is the rate of initiation for which an Arrhenius relationship is appropriate. Also, the rate of depolymerization can approach that of polymerization at elevated temperatures. In the case of methacrylate polymerization, however, at the temperatures of interest, the rate of depolymerization is believed to be sufficiently small to allow the effect to be negligible.[16]

As increasing temperature lowers viscosity, the diffusion of radical ends is increased and the prop-

agation rates are reduced. Conversely, the increased temperature allows a greater concentration of monomer in solution, which results in a higher molecular weight polymer being formed.

The effect of increased initiation rate with temperature can be compensated in two ways: First, an alternative initiator with a longer decomposition half-life may be used. Second, the sequential addition of initiator in aliquots will reduce the initiating radical flux. The results obtained indicated that, at equivalent concentrations, a higher initiating rate obtained at elevated temperatures resulted in lower polymer molecular weight.

Effect of Initiator Concentration on Molecular Weight and Yield

Assuming no chain transfer to initiator, the molecular weight is simply proportional to the inverse square root of initiator concentration. However, data obtained show that a more complex relationship arises. First, low initiator concentrations (less than 0.2 mol %) always give a low yield. Above this, there is a dramatic increase to its maximum value. At low yield, both yield and molecular weight is solvent-dependent. Also, when both yield and molecular weight are low, an increase in monomer concentration at the same initiator concentration results in a decreased yield. Analysis of these results requires an understanding of various competing effects and their relative degree of influence. First, the low yield may be explained by the fact that there is a small amount of inhibitors or retarders present in the polymerization—from glassware, monomer, or solvent. The presence of inhibitors in both solvent and monomer is substantiated by the fact that an increase in monomer concentration at the same initiator concentration further decreased the yield and that the yield and molecular weight was also solvent-dependent. To investigate the existence of initial inhibition during polymerization, the rate of formation of polymer was plotted as a function of time (Fig. 5).

The results indicate that inhibition occurs for the first 60 min, which corresponds to the consumption of about 0.7 mol % of initiator. After that, there may be slight retardation, but the overall rate appears to show typical polymer behavior. The cause of this inhibition was investigated and oxygen was shown to be a major inhibitor for the methacrylate monomers.

The solvent dependence at low initiator concentration can be analyzed in various ways: First, the
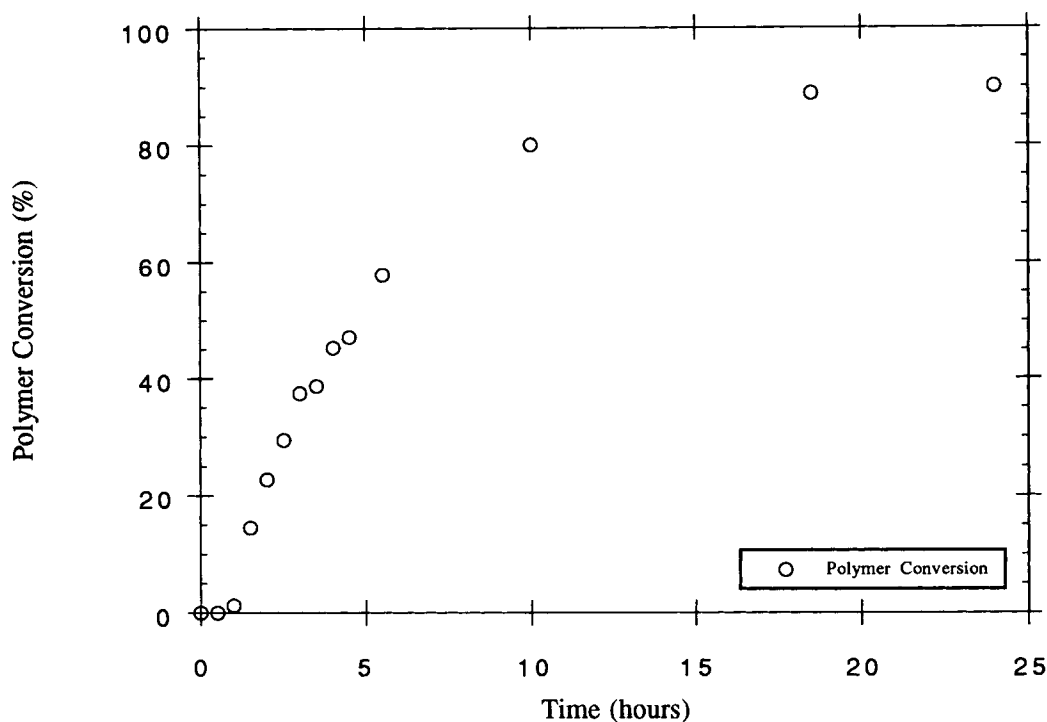
Figure 5   Polymerization rate as a function of conversion. Data obtained by GPC.

initiator efficiency is solvent-dependent. This is due to the cage effect[17] that results in initiating radical recombination. Hence, if the initiator concentration is low and there is significant inhibition, then the yield may be sensitive to initiator efficiency. The molecular weight dependence on solvent at low yield may be explained by both chain transfer to solvent and viscosity-dependent diffusive effects. At low initiator concentrations, lower chain-transfer constant solvent increased both the yield and molecular weight.

Cross-linked Polymers

To avoid process problems such as high solution viscosity and poor filtration, associated with high molecular weight polymer, chemical cross-links were introduced into the film by chemical reaction after filtering and spin-coating. Two different techniques, one by high-energy radiation[18] and the other by cross-linkable monomers and dopants, were employed.

In the high-energy radiation experiments, powder samples and spin-coated films (< 1 μm thick) of NLO copolymer were exposed to E-beams up to 40 Mrad. However, the results obtained from both spectral and GPC data suggested that neither cross-

linking nor degradation of the NLO polymer chains occurred.

A small amount of acrylic monomer with a pendant functional group amenable to chemical cross-linking was also incorporated in the copolymer, resulting in a cross-linkable terpolymer. The polymerization of hydroxyethyl methacrylate monomer with an NLO chromophore containing methacrylate monomers provided polymer chains with randomly distributed hydroxyl groups that are available for cross-linking. A curing agent, diisocyanatohexane, was then mixed with the terpolymer solutions prior to the spin-coating process, allowing cross-linking reactions to be carried out during the drying process. Qualitative estimations of the resultant film showed an improvement in mechanical behavior over non-cross-linked samples.

PROCESSING

Formation of Cracks in NLO Polymer Films

The premature crack formation in polymers at stresses considerably below the nominal yield stress, while in contact with aggressive environments, is called environmental stress cracking. Solvent stress cracking is a result of enhanced craze growth and

breakdown by the influence of a solvent on a polymer film, already under residual tension.[19,20] This problem is encountered when multilayer films are prepared sequentially. The localized release of forces around flaws causes an unbalance of the forces already under residual stress, bringing the onset of crack formation. Each polymer layer is subsequently exposed to solvent during the device fabrication, thus increasing the cracking tendency. Short drying intervals were shown to postpone cracking because the partially dried film is still in a rubbery state on contact.

The tendency of solvent cracking in polymers under stress is known to be a function, to a first approximation, of the difference between the solubility parameter of the polymer and of the solvent.[19] Various solvents were employed in the film preparation process. However, the cracking initiation and propagation rates are so fast for film under the residual stress that no solvent proved to be suitable for both dissolutioning the polymer and crack prevention.

Residual Stresses

Polymeric coatings tend to shrink as they dry due to physical changes occurring on solvent evaporation. However, the area of the coating is constrained to remain at its original wet size by adhesion to the rigid substrate; thus, volume changes are accommodated by changes in thickness accompanied by fluid flow. After the coating has solidified and can no longer flow, further solvent loss produces an internal strain in the plane of the film as it proceeds to its final dry state. Unfortunately, this internal residual strain seldom disappears completely after the normal viscoelastic relaxation process of the polymer but remains to threaten the cohesive and adhesive properties of the system.[21-23]

Internal strain energy stored in a film increases with thickness and, at a certain thickness, that energy is sufficient to overcome its cohesive or adhesive strength.[24] If the cohesive failure stress is below that produced by the internal strain, then stored internal strain energy will be released by cracking rather than by adhesive failure. This is the case when NLO polymer solutions are spun and dried below the glass transition temperature of the polymer.

These observations indicate that the magnitude of the internal shrinkage stress is related to the time scale of the chain relaxation during the drying process of the polymer film. As solvents evaporate, the T_g of the polymer coating increases, free volume de-

creases, and the rate of solvent loss becomes dependent on the diffusion rate of solvent to the film surface. As solvent loss continues, the T_g of the polymer coating approaches the temperature at which the film is being formed. From this concentration in the coating, large-scale molecular motion of the polymer chain does not take place, and, thus, the rate of solvent loss becomes very low and the rate of chain relaxation to relieve the internal stress becomes extremely slow. To facilitate polymer stress relaxation, it is necessary to heat the film to a temperature above the T_g of the solvent-free polymer.

On heating a polymer coating above the T_g in the drying process, thermal stress[22] is introduced into the dried film. During the cooling stage, thermal stresses arise in the film due to the difference in the thermal expansion coefficient between polymeric films and inorganic substrates. Since the contraction of the top layer in the film is greater than that of the bottom layer, which is constrained to contract along with the substrate, tensile stresses are introduced. These thermal residual stresses in the NLO polymer are usually of sufficient magnitude to cause thicker films (> 10 μm) to crack spontaneously or to show solvent stress cracking.

The use of polymeric substrate instead of a silicon wafer often prevents the introduction of the stresses into the NLO polymer film. However, this introduces several device fabrication process problems. These include warping of the substrate during electroplating and baking, dissolving of the polymeric substrate by solvents used in spin-coating and lithography, as well as cracking of a thin metal electrode layer that is sandwiched between the polymeric substrate and film.

For a thick polymer film, thermal stresses are induced by rapid cooling from above the glass transition. During cooling, the surface of the film is transformed to a rigid glass while the inside of the film is still above its glass transition. The result is differential contraction between the surface and bulk due to their different coefficients of thermal expansion. This type of thermal stress may be relieved by careful design of the drying procedure.

Plasma Polymer Barrier Layer

In another attempt to prevent solvent cracking during the spin-coating process, solvents were blocked from making contact with the previously cast film by a vacuum-deposited plasma polymer layer. Typically, a few hundred angstroms-thick plasma polymer was used as a barrier layer. Plasma polymer-

ization is a well known and suitable method for preparing thin and defect-free films that adhere well to any substrate. This plasma barrier layer is dense enough to prevent penetration of solvent, yet thin enough not to interfere with guided waves in the NLO polymer film.

A 300 Å-thick plasma polymer from CH_4 was coated on an NLO copolymer film. When cyclohexanone was spread over the plasma film surface, only the portion of the film not covered with the plasma polymer layer showed cracks. Even a plasma polymer layer as thin as 100 Å was effective as a solvent barrier for the spin-coating process. In this technique, the surface properties of the film were able to be modified depending on gases used in the plasma process. When hexamethyldisiloxane was used to form a plasma layer on the NLO film, the hydrophobic film surface characteristic of the film could be obtained. This hydrophobic film surface was also shown to be effective as a barrier layer against solvent cracking.

Plasma technology was found to provide a way to achieve continuous vertical integration of optical devices without any cracking problems in future applications and is a promising technique.

CONCLUSIONS

Four main causes of cracking during the fabrication process were the brittle nature of the NLO polymers, their low molecular weight, the residual stresses, and the solvent stress cracking. The brittle nature of the NLO polymers arises from two main material characteristics: low molecular weight and the absence of a secondary relaxation. Extensive synthetic work and analysis of the relevant parameters revealed that a maximum molecular weight was obtained by increasing the monomer concentration to its maximum obtainable value at a temperature that allows the initiator to have a half-life of about 4 h. The initiator should be added in aliquots to minimize the radical flux, and the solvent should have low chain transfer and good solvating properties for the monomer. By increasing the molecular weight above a critical entanglement length, an improvement in the mechanical behavior was observed empirically by film analysis and viscoelastic data. Direct mechanical analysis was not carried out because free-standing films are not self-supporting. Although the crack resistance can be improved by forming entanglements and results indicated that larger film thicknesses could be supported, the high molecular weight polymers result in a processing problem due to their high solution viscosity.

Polymeric substrates as an alternative to silicon substrates were used in order to reduce the residual thermal stresses arising from the difference in thermal contraction between the polymeric film and inorganic substrate. Although this approach is effective in reducing the residual stresses, it has its own processing problems during the fabrication process, such as warping of the polymeric substrate as it is heated close to the substrate glass transition and cracking of thin metal electrode layers. This warping was shown to be reduced as the substrate glass transition was increased. Annealing or drying films at high temperature also helps in reducing the residual stresses in the films. However, this approach initiates thermal degradation of the polymers and results in thermally cross-linked material. These resultant inhomogeneities give rise to serious application problems.

It was found that deposition of a thin plasma polymer layer on the NLO film surface prevented solvent contact and stopped solvent-induced cracking. Since the thickness of the plasma barrier layer is in the range of a few hundred angstroms, the waveguide optics were not affected. This plasma technique is a simple method that can be conveniently employed in the fabrication process.

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