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Thermally Reversible Polymer Linkages. 3. Covalently Cross-Linked Poly(azlactone)

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ABSTRACT: Research on the azlactone–phenol reaction has been extended to cross-linking chemistry. Poly(2-vinyl 4,4-dimethyl-2-oxazolin-5-one) was used to synthesize three-dimensional networks using bisphenol cross-linkers. Among the bisphenols considered, only bisphenols containing electron-withdrawing groups at the site para to the phenol hydroxyls cross-link the polymer. The bisphenol 4,4′-(perfluorobutanediyl-1,4-disulfonyl)diphenol was also found to facilitate the reverse reaction in high-boiling solvents, re-forming linear polymer and bisphenol at temperatures below the degradation temperature of the linear polymer. These networks undergo up to 20 or more cycles of cross-linking–de-cross-linking both inside and outside of the drybox.

Introduction

Prior research[1-3] has shown that azlactones (2-oxazolin-5-ones) are suitable electrophiles for thermally reversible ring-opening reactions with phenols containing electron-withdrawing moieties at the position para to the phenol hydroxyl. Linear stepwise addition polymers were formed from 1,4-tetramethylenebis(2-oxazolin-5-one), a bisazlactone, and 4,4′-bisphenols with electron-withdrawing moieties between the phenol groups. The bisphenols with electron-withdrawing functionalities were also found to facilitate the reverse reaction to re-form the monomeric species at about 200 °C.[3] Problems with this system were encountered in the low yield of stepwise polymerization chemistry, leading to low molecular weights. In addition, degradation at the high temperatures required for the reverse reaction caused failure to re-form polymer after heating.

These results suggested than an analogous network-forming system of azlactone-functionalized polymer and bisphenol cross-linker might fare better in this reaction scheme than the linear polymerizations. While good yield is essential to achieve high degrees of polymerization in a stepwise reaction, only a few percent cross-linking is sufficient to achieve an insoluble network.[4] By the same reasoning, cross-link–de-cross-link cycling is also a good possibility for this system, since the cross-linking forward reaction should also be more tolerant of any degradation that occurs.

This paper describes the cross-linking reactions of poly(2-vinyl-4,4-dimethyl-2-oxazolin-5-one) or poly(vinylazlactone) (I), with 4,4′-bisphenols II in solution at ambient temperature, and describes how the cross-linker IId also facilitates the reverse reaction to re-form IId and linear I below 200 °C. This reaction scheme is shown in Figure 1. It was found that the forward and reverse reactions exhibited many of the same trends of reactivity as were found during examination of the corresponding model studies and polymerizations.[1-3]

The cross-linking reaction scheme was chosen such that the effect of various substituents on phenol monomers could be studied. Polymer I was a convenient choice as it is easily polymerized by known methods[5] and has minimum steric bulk at the 4-site of the azlactone so as to eliminate facile acid–base chemistry. Bisphenols IIa–d were chosen for the purpose of comparing the effects of electron-withdrawing groups to Bisphenol A (IIa; 4,4′-isopropylidenediphenol), which contains no electron-withdrawing capability. These are the same bisphenols as used in the corresponding linear polymerizations with bisazlactones.[3]

Background Information. Thermally reversible covalent cross-linking, as opposed to thermally reversible chain extension, has been studied with relative success. Even so, only five such systems are currently found in the literature which describe thermally controlled covalent network formation.[6-20] Most of these systems are not commercially useful due to either degradation problems or insufficient reactivity of the de-cross-linking reaction to re-form linear polymer.

Experimental Section

General Information. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile (MeCN) used for reaction solutions were distilled and

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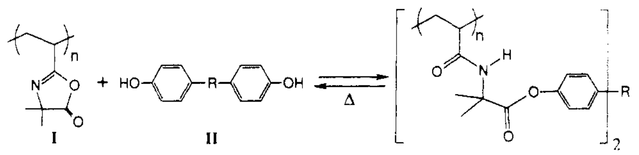


R	Compound name
	**IIa**: 4,4'-isopropylidenediphenol.
$-\overset{O}{\underset{O}{S}}-$	**IIb**: 4,4'-sulfonyldiphenol.
$-\overset{CF_3}{\underset{CF_3}{C}}-$	**IIc**: 4,4'-hexafluoroisopropylidenediphenol.
$-\overset{O}{\underset{O}{S}}-(CF_2)_4-\overset{O}{\underset{O}{S}}-$	**IId**: 4,4'-(1,4-disulfonylperfluorobutane)diphenol

Figure 1. Cross-linking scheme for poly(2-vinyl-4,4-dimethyl-2-oxazolin-5-one) (I) and bisphenols II.

stored in the drybox unless otherwise indicated. THF was distilled from Na–K alloy with benzophenone indicator. DMF and DMSO were fractionated in vacuo using standard Schlenk techniques. MeCN was distilled from calcium hydride over argon. All other chemicals were obtained and used without further purification unless noted.

Some reactions were performed in a Vacuum Atmospheres Dri-Lab Model HE-43-4 drybox under an argon atmosphere and equipped with a Model HE-63-P pedatrol pressure regulator and large-capacity vacuum pump. The atmosphere in the drybox tested dry to diethylzinc and titanium tetrachloride and so was maintained at ≤10 ppm H_2O and O_2.

Infrared spectra of polymers were run on a Perkin-Elmer Model 281 spectrophotometer by casting a film from HPLC-grade CH_2Cl_2 onto quartz windows. Evaporation of the solvent was accomplished by applying a vacuum for about 1 h at room temperature.

Size-exclusion chromatography (SEC) was performed on a Waters Model 6000A liquid chromatograph equipped with a differential refractometer, a Perkin-Elmer Model LC-75 UV detector at the specified wavelength, and SEC columns as indicated. The flow rate was 1.0 mL/min with THF as the mobile phase. Calibrations and molecular weight determinations were performed using a Zenith Data Systems PC.

HPLC traces were obtained on a Waters Model 590 instrument equipped with a Kratos Spectroflow 757 UV detector set at the specified wavelength, a Perkin-Elmer LC-25 refractive index detector, and a Waters Nova-Pak C18 reverse-phase column. The mobile phase was 60% aqueous CH_3CN, at a flow rate of 0.5 mL/min. Sampling was accomplished by removing 10-μL aliquots of the solutions and diluting immediately in 2 mL of HPLC-grade CH_3CN. Peak areas were determined by cutting and weighing. All SEC and HPLC samples were prefiltered with 0.45-μm Millipore filters.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 instrument equipped with a N_2 purge, a TAC7 data analysis package, and a PE 7500 data system; indium and lead were used as standards. Thermogravimetric analysis (TGA) was obtained using a Perkin-Elmer TGA 7 with N_2 purge; the instrument was equipped with TAC7 data analysis and a PE 7500 computer. Alumel and Nicoseal (Perkin-Elmer) were used as standards for Curie point magnetic transitions.

Synthesis of Starting Materials. Poly(2-vinyl-4,4-dimethyl-2-oxazolin-5-one) (I) was obtained by literature methods.[5] Bulk polymerization of freshly distilled 2-vinyl-4,4-dimethyl-2-oxazolin-5-one[21] was carried out at 50 ± 2 °C with AIBN to give polymer Ia. Using TSK G3000 and TSK G5000 SEC columns (THF, 1.0 mL/min), the molecular weight of Ia was determined by polystyrene standards (M_w values of 17 500–800 000) to be $M_w \sim 2 \times 10^6$, with a polydispersity index (PDI) of ~3. Refractive index detection was used. Characterization of the azlactone functionality was via IR and confirmed by known absorptions as described in the literature.

Lower molecular weight polymer Ib was synthesized using THF as a chain-transfer agent as described in the literature.[22] Using 20 g of freshly distilled monomer, 80 g of freshly distilled THF, and 1.0 g of AIBN, a polymer of M_w = 75 000, PDI = 2.1, was obtained using SEC measurements as described above for the bulk polymer. Functional group characterization was by IR. Both polymers were stored in the drybox to prevent hydrolysis of azlactone moieties.

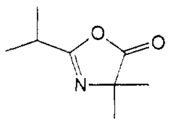


Figure 2. Model azlactone 2-isopropyl-4,4-dimethyl-2-oxazolin-5-one (III). The isopropyl group was used to mimic the polyethylene backbone of polymer I.

Bisphenols IIa–d were used for the cross-linking of I. Bisphenols IIa (4,4'-isopropylidenediphenol or Bisphenol A), IIb (4,4'-sulfonyldiphenol or Bisphenol S), and IIc (4,4'-(hexafluoroisopropylidene)diphenol or Bisphenol F) were used as obtained from Aldrich. They were brought into the drybox after applying vacuum overnight (40–80 °C) to remove adventitious water.

Bisphenol IId, 4,4'-(perfluorobutanediyl-1,4-disulfonyl)diphenol, was synthesized from a fluorophenyl precursor. The precursor was obtained from E. I. du Pont de Nemours and Co.[23] The transformation to IId is described elsewhere.[3]

Model Studies. Equilibration studies in MeCN solution were performed with 1 equiv of II and 2 equiv of a model azlactone, 2-isopropyl-4,4-dimethyl-2-oxazolin-5-one (III). The structure of III is shown in Figure 2; its synthesis is described elsewhere.[1,2] The solutions were made as concentrated as possible. HPLC analysis was used to determine the reaction products. A typical solution was mixed in the drybox as follows:

reagent	amount
III	0.115 g (7.42×10^{-4} mol)
IIc	0.125 g (3.72×10^{-4} mol)
MeCN	to 0.70 mL

The uncatalyzed solutions of II and III were placed in small (1–2 mL) heavy-walled glass vessels equipped with high-pressure stopcocks. Equilibration at various temperatures was allowed until it was confirmed by HPLC that equilibrium had been reached. Temperature was regulated by an oil bath between 27 and 120 °C; at temperatures over 120 °C, the reaction vessel was removed (stopcock closed) from the drybox and placed in a salt bath regulated at the desired temperature ±3 °C. The salt bath consisted of a mixture of 40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3 which was placed in a glass dish and heated, with magnetic stirring, on a hotplate. This mixture melts at about 140 °C.[24]

Cross-Linking Reactions. Both the forward and reverse cross-linking reactions were studied. Polymers Ia ($M_w \sim 2 \times 10^6$, PDI ~ 3) and Ib (M_w = 75 000, PDI = 2.1) were used in the experiments with bisphenols IIa–d.

Cross-Linking Forward Reaction. Polymers I were dissolved at maximum concentration in THF, DMF, or DMSO along with the specified bisphenol II as shown for a typical solution mixed inside the drybox:

reagent	amount
Ia	0.070 g
IIc	0.025 g (0.15 equiv, or 15%)
DMF	to 1.0 mL

The number of equivalents of cross-linker was determined by dividing the measured mass of either polymer by 139 g/mol, which is the molar mass of one repeat unit. Assuming no hydrolysis of azlactone groups, this gives the total moles of the azlactone functionality. The desired number of equivalents of II was then calculated based on moles of polymer repeat units. Percent II is this number multiplied by 100. Solutions with 0.02–0.50 equiv (2–50%) of II were mixed in this fashion.

These solutions were allowed to stir in vials or round-bottom flasks inside the drybox or under an argon blanket. Gelation was determined by the point at which the stirbar could no longer stir the solution, and swirling of the vial revealed a swelled, insoluble material. Control solutions of polymer in the absence

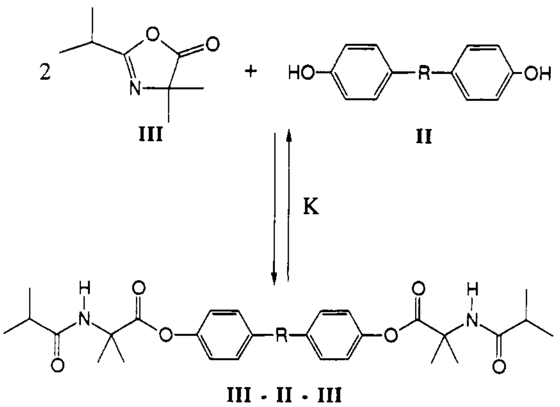


Figure 3. Reaction scheme for the model study 2(III) + II, used to predict the reaction behavior of II with polymer I.

of cross-linker were run alongside all cross-linking solutions to determine that gelation did not occur in the absence of II.

Confirmation of gelation was made by filtering the insoluble material from solution and washing several times in fresh THF. The contents of the THF wash were analyzed by SEC to determine whether soluble I existed.

Reverse Reaction (De-Cross-Linking) and Cycling. The reverse reaction was examined in several ways. The gels swelled with solvent were observed for the disappearance of the gel upon heating: both the linear polymer V and the bisphenols VI are soluble in all of the solvents used. Therefore, the mixtures were examined for formation of solution during heating, and the persistence of the solution thus formed upon cooling to ambient temperature. In some cases the networks were washed and dried as described above and heated in the absence of solvent; alternatively, solvent could be added back after drying.

TGA and DSC runs were performed on the networks in the absence of solvent, using a temperature ramp of 10 °C/min from 40 to 400 °C or 450 °C under a N_2 blanket. The washed and vacuum-dried networks were also returned to the drybox and examined in sealed vials or in high-pressure vessels. The networks were heated at the desired temperature in a sand bath or salt bath, either neat or with solvent added back. The neat reactions were cooled and extracted with solvent, and the wash was examined by SEC.

Cycling experiments were performed for all insoluble networks observed to undergo the reverse reaction after initial cross-linking. All the cycling experiments were carried out in DMF or DMSO. The time required for the mixture to form a gel was noted; the solution was then heated for the amount of time necessary to re-form a solution which persisted after cooling the flask to ambient temperature. The solution was allowed to stir at ambient temperature until gelation was again observed. Cycling was repeated until gelation was not observed for 2 weeks after heating.

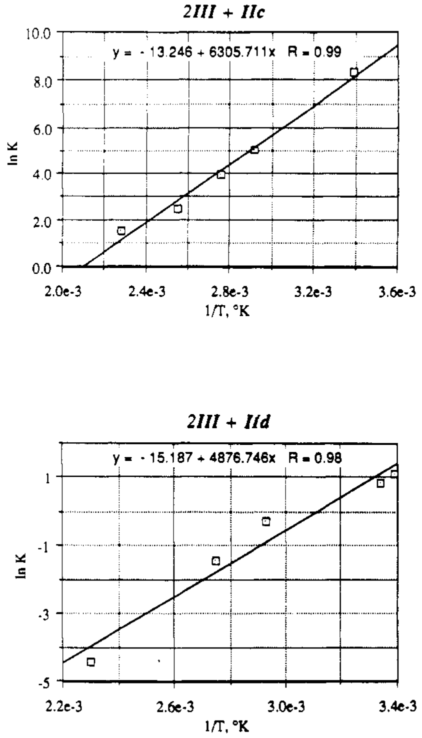
Results and Discussion

In order to determine the equilibrium constants for the reaction of bisphenols II with azlactone, all compounds II were equilibrated with 2 equiv of the model compound III at several temperatures between 22 and 165 °C. The reaction scheme is picture in Figure 3. In these experiments, solutions in MeCN were equilibrated and the reactions monitored by HPLC with UV detection.

Equilibrium constants and enthalpies for the reactions of II with 2(III) were calculated as shown in eqs 1 and 2.

$$K = [\text{III–II–III}]/[\text{II}][\text{III}]^2 \qquad (1)$$

$$d(\ln K)/d(1/T) = -\Delta H°/R \qquad (2)$$



T, °C	K, l²/mol²
22	4.17×10^{3}
71	1.51×10^{2}
91	5.10×10^{1}
119	1.19×10^{1}
165	4.64×10^{0}

ΔH° = 52.4 kJ/mol

T, °C	K, l²/mol²
22	2.99×10^{0}
26	2.29×10^{0}
68	7.61×10^{-1}
91	2.42×10^{-1}
162	1.19×10^{-2}

ΔH° = 40.5 kJ/mol

Figure 4. Equilibrium constants and enthalpies of reaction for the reactions of 2(III) with IIc and IId as noted.

It was assumed that the UV molar absorptivities of all absorbing species (II, III–II, and III–II–III) are the same, since the products were not isolated for separate measurements. The integrations of the separate peaks due to II, III–II, and III–II–III were calculated to determine their relative amounts, and equilibrium constants were then calculated as follows. The concentration of unreacted azlactone III, which absorbs only very weakly in the UV, was calculated by taking the initial concentration of III and subtracting the sum of the concentration of III–II plus twice the concentration of III–II–III. The equilibrium constant then is calculated using eq 1. By equilibrating these solutions at various temperatures, ΔH° for the reaction was measured as in eq 2.

The solution of IIa and III did not undergo any discernible reaction after 1 week and so was not studied further. The solutions with IIb and III underwent extensive precipitation and so could not be measured. The unreactive nature of bisphenol IIa agreed well with the prediction that bisphenols without electron-withdrawing groups do not undergo facile reaction with azlactones in the absence of catalysts.

Equilibrium constants and enthalpy values for reactions of bisphenols IIc and IId with 2(III) are shown in Figure 4. On the basis of these measurements, it was predicted that cross-linker IId held the most promise for the successful reversible reaction in this system: at 22 °C, the equilibrium constant is low but probably sufficient to yield a gelled network polymer. At 165 °C, III–IId–III was nearly depleted; some III–IId remained. IIc did react to a much further extent than IId at ambient temperature, which may be important for network formation. However, a substantial amount of III–IIc–III remained in solution after equilibration at 165 °C. Therefore, IIc may not be suitable for the de-cross-linking reaction.

It would be pertinent to perform equilibrium measurements starting with the purified III–II–III type compounds. In this manner, it would be confirmed that the equilibrium constants that were measured were in fact true equilibria. However, difficulties in purification arose when II, III–II, and III–II–III were present in the same solution. Although it may be possible to separate these components by bulk column chromatography, this was not attempted. It was felt that purified III–II–III compounds might not be stable (due to the difficulties encountered upon

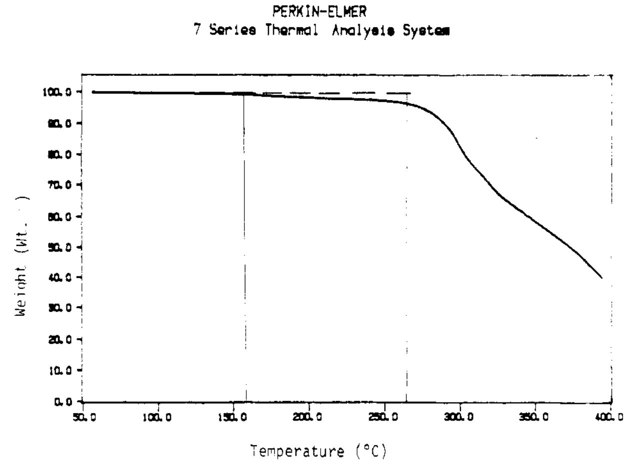


Figure 5. TGA trace for polymer Ia. The temperature ramp was run at 10 °C/min.

Table I
Results of Cross-Linking Reactions of II with Polymer Ia in THF[a]

bisphenol	% II	gelation, h	bisphenol	% II	gelation, h
IIa	3	no	IIc	3	no
IIa	15	no	IIc	15	24–48
IIa	50	no	IIc	50	3
IIb	3	no	IId	3	~48
IIb	15	no	IId	15	24
IIb	50	24–48			

[a] All reactions were run in the drybox or under an argon blanket.

attempting to purify them by other means), and either hydrolysis of the ester linkage or the reverse reaction could spontaneously occur at ambient temperatures.

Cross-linking of polymer Ia ($M_w \sim 2 \times 10^6$, PDI ~ 3) with bisphenols II was undertaken. Reactions were run in THF, DMF, and DMSO solutions. Initially, these reactions were performed in the drybox.

The indications from the linear polymerizations were that Lewis acids and bases did not aid in the forward reaction,[3] as was the case in small-molecule model studies.[1,2] Additionally, these catalysts promoted degradation of the solutions upon heating and so were not used in these studies. The polymer is basically a functionalized polyethylene and so is fairly susceptible to thermal degradation even without catalysts. TGA studies of Ia, shown in Figure 5, indicate that degradation begins at about 160 °C in nitrogen, with major degradation starting at about 270 °C. No further degradation studies were needed for the polymer, since polymers cannot be vaporized without degradation due to their high cohesive energy densities.[25]

Thus, the uncatalyzed reaction solutions were not to be heated above 160 °C in order to avoid degrading the polymer, although temperatures of up to 200 °C could possibly be tolerated for short periods of time. It is possible that the reverse reaction, if run at temperatures greater than 200 °C, could be followed by re-cross-linking; however, the best chance of cycling the system is realized by keeping temperatures below 160 °C.

The solvent used initially for the cross-linking forward reactions of Ia was THF. Solutions were generally 0.07–0.09 mol/L in Ia. The reactivities of the bisphenols II were easily differentiated by using varying equivalents of II and noting the time required to yield an insoluble gel with Ia. Results of the forward reaction in THF are shown in Table I. Note that "no gelation" indicates that a gel was not observed over a 14-day period at ambient (26–27 °C in the drybox) temperature.

Two distinct trends were recognized upon inspection of Table I. The first notable result was seen when each of the bisphenols II were used at 3% (0.03 equiv). The only bisphenol observed to gel Ia was IId at this low percent of cross-linker. This was an unexpected result based on both the model study of IId and 2(III) as well as linear polymerizations with bisazlactones and bisphenols.[3] In both cases, bisphenol IId showed a relatively low reactivity.

However, upon inspection of the individual structures of the bisphenols, it can be seen that IId has more flexibility between the phenol rings than IIa–c. This may be the key to its observed reactivity in cross-linking the polymer in THF solution. The cross-linking reaction differs from all others studied thus far: small azlactone molecules (i.e., III or a bisazlactone) may diffuse through a solvent to undergo reaction; however, azlactone functionalities attached to a polymer backbone are restricted in their movement by the rest of the chain. The bisphenols II are small molecules, yet, upon the reaction of one hydroxyl functionality, the other reaction site is "anchored" to the polymer chain. Therefore, the flexibility of the small-molecule cross-linker may be more important in the cross-linking reaction than in the model studies or the polymerizations.

Another result of these studies is that the relative reactivities of bisphenols can be compared by varying the number of equivalents of bisphenol cross-linker. For example, at 15% II, it can be seen that IId gelled the polymer Ia in 24 h, followed by IIc in 24–48 h, followed by IIb and IIa, which did not yield a gel after 2 weeks. Likewise, at 50% cross-linker, IIc gelled polymer Ia in 3 h, followed by IIb at 24–48 h; IIa did not gel Ia. Relative reactivities of bisphenols II in the cross-linking forward reaction can thus be assigned as IId > IIc > IIb ≫ IIa.

Swelling numbers were obtained for some of these networks, as well as percent extractables. The percent extractable is the initial mass of the polymer plus cross-linker, minus the mass of the network after exhaustive washing to remove soluble materials, followed by drying to remove solvent. In other words, this should measure the total percentage of un-cross-linked material from the mixture. Percent extractables is expressed as the percent mass lost from the original mass of the polymer plus cross-linker (after washing and drying insoluble materials). Percent swelling is the percent mass uptake of solvent relative to the theoretical mass of the dried network.

Both swelling and extractables were measured using THF after 24 h of reaction time. Polymer Ia was reacted with 3% IId, 15% IId, and 15% IIc, as the three networks so formed should differ in their percent swelling and/or percent extractables. However, no real differences could be detected using either of these methods. All the networks swelled to 900–1000% in THF, or 9–10 times the dry weight. Extractables ranged from 22% with 15% IIc to 27% with 15% IId. Thus the measurement of swelling or extractable materials was not thought to be a good method to indicate the differences between the networks formed using varying types and amounts of cross-linkers.

This would also seem to indicate that the extent of cross-linking in all cases is similar. This may be due to the nature of the polymer network formation: at a certain percent of cross-linking, soluble materials (i.e., unreacted I or II) may not have enough mobility to move through the insoluble network to give further cross-linking. This would explain the observations of similar network behaviors at the varying levels and structures of II.

The reverse reaction was attempted for these networks after 3–7 days of reaction time in THF. Heating was carried out in THF solution, in sealed vials inside the drybox. Temperatures of 150–180 °C were used. Upon heating, every network in THF was observed to undergo "precipitation" from solution. Although not a true precipitation, the network material was observed to become completely insoluble or "deswelled" in the THF solvent, as evidenced by the formation of a collapsed, solid white mass where a transparent swelled mass could formerly be seen at ambient temperature. This occurred about 1 min after the samples were immersed in an oil bath—apparently as soon as the THF exceeded reflux temperature in the small vessels. When the phenomenon was carefully observed, it seemed that reflux occurred first, followed by precipitation about 10–15 s later. Although the mixtures were heated for up to 24 h, the solid mass never dissolved or swelled. Additionally, upon returning the mixtures to room temperature, the deswelled network was not observed to return to a swelled state.

It was suggested[26] that the network had exceeded the lower critical solution temperature (LCST), a common occurrence for linear polymers in a solvent under pressure and above the boiling point of the solvent.[25] Although these particular samples contained only a minor amount (if any) of linear polymer, it seems reasonable that the "deswelling" observed could be the same phenomenon as would apply to a swelled network.

Another possibility is that the swelled networks, with increased mobility at elevated temperatures, can undergo further cross-linking reactions and thus become completely insoluble. If some finite amount of cross-linking is physically possible at ambient temperature, it may be that "equilibrium" for the reaction is not approached. By increasing the mobility of all the constituents of the reaction, further cross-linking may be allowed at elevated temperature.

TGA and DSC were also used to examine the networks formed with polymer Ia and 50% IIb–d in THF for evidence of the reverse reaction. The networks were washed thoroughly with THF and dried before testing. It was hoped that, in this manner, the reverse reaction would be observed in the absence of solvent.

TGA traces revealed only that weight loss (from either degradation of the polymer backbone or reversibility followed by vaporization of cross-linkers II) took place at slightly higher temperatures than for linear Ia alone. Inspection of the TGA traces of IIb–d alone revealed that the weight losses observed for the networks could not be attributed to vaporization of the cross-linkers: vaporization and/or degradation of all II occurred at higher temperatures than the transitions seen for their respective networks with Ia. Thus no useful information was obtained from this study.

DSC, while thought to be the ideal method for examining reversibility of the network to form linear polymer and cross-linker, also did not reveal any transitions indicating such a reaction was taking place. Additionally, the DSC pans burst during heating so no information was obtained regarding other characteristics of these networks.

It was thought that by using higher boiling solvents for the solution reactions reversibility could be observed in solution without the deswelling problems seen in THF. DMF and DMSO came to mind as solvents that boil in the range where the reverse reaction is expected to occur (153 and 189 °C, respectively). Both of these solvents were found to dissolve the polymers Ia and Ib and all bisphenols II, although DMSO took several hours to dissolve the polymer. For polymer Ia, solutions ranging from 0.07 to 0.10 g/mL were attainable in both solvents. Polymer Ib could be used at about 0.20 g/mL. Reactions were initially performed in the drybox with fractionated solvents.

In both of the high-boiling solvents, gelation of the polymers with IIb–d occurred with a somewhat different reactivity from the THF solutions. For example, a solution of 0.09 g/mL of Ia in DMF was cross-linked by 5% IIb–d within 2 h with IIb and IIc and in about 18 h with IId. IIa did not cross-link the polymer, as was expected. When the solutions with Ia were diluted with additional solvent, this had the effect of slowing the cross-linking reaction in all cases and caused failure in the solutions where 5% or less of II was used.

The rates of gelation were different from those observed for the THF cross-linking solutions, where IId was the most reactive bisphenol. Apparently the reaction in DMF is controlled by equilibrium constants, similar to the measurements of IIc + 2(III) and IId + 2(III) in MeCN. The model predicted that the reaction of III with IIc is shifted further to the right than IId. This trend appears to be followed in the case of the DMF and DMSO solutions. If this is also the case for the de-cross-linking reactions, then IId offers the best possibility for reversibility of the gel to form linear I and IId.

The solutions of 0.09 g/mL of Ia and 5% IIb–d in DMF were then heated to reflux in sealed vials and carefully observed to see if the gel became soluble. For the networks formed with both IIb and IIc, the gel persisted at the reflux temperature of DMF. However, the gel of Ia and IId was observed to become soluble 1–3 min after DMF reached reflux. Upon cooling to ambient temperature the solution persisted: stirring was smooth, and the solutions were of the same apparent consistency of that upon mixing. Gelation subsequently occurred in this solution after about 18 h, which is the same as for the initial reaction.

Although it is possible to form dimethylamine in refluxing DMF, this possibility was believed to be minimized. Certainly in the case of reactions run inside the drybox, there was minimum water available for hydrolysis type reactions. Even outside the drybox, reflux was maintained for ≤5 min and the mixtures were blanketed with argon.

An SEC experiment, shown in Figure 6, was performed outside of the drybox (argon blanket) to determine whether the cross-linking was chemically reversing or whether some other phenomenon was causing the observed dissolution of the gelled network. An aliquot of Ia with 15% IId in DMF was removed upon mixing and immediately diluted in THF. This sample was subjected to SEC analysis. The presence of Ia was noted as well as the ratio of IId:DMF.

The rest of the solution was allowed to react for 24 h at 22–23 °C under an argon blanket, after which a sample of the swelled gel was removed and washed in THF to remove soluble material. The THF wash was also passed through the SEC. The absence of polymer was noted, along with the decreased ratio of IId:DMF. The ratios of IId:DMF were then used to determine the amount of cross-linker IId taken up after 24 h of reaction time. This turned out to be 27% of IId added to the solution initially or 4% (0.04 equiv) IId taken up. It is not known how much IId was reacted on both sides, forming cross-links, and how much was reacted on only one side.

Finally the gel in DMF was heated sufficiently to form a solution, and upon cooling another sample was removed and diluted in THF. Again, the sample was analyzed by SEC. Ia was once again observed, along with most of IId. The ratio of IId:DMF indicates that the majority of the cross-linker is once again soluble in THF. The polydispersity increased in the mixture returned after heating, which may indicate that some degradation or redistribution via chain scission had taken place upon heating. Most of the increase in polydispersity was due to lower molecular weight material formation. However, the polymer so formed is still soluble in DMF and undergoes re-cross-linking smoothly at ambient temperature.

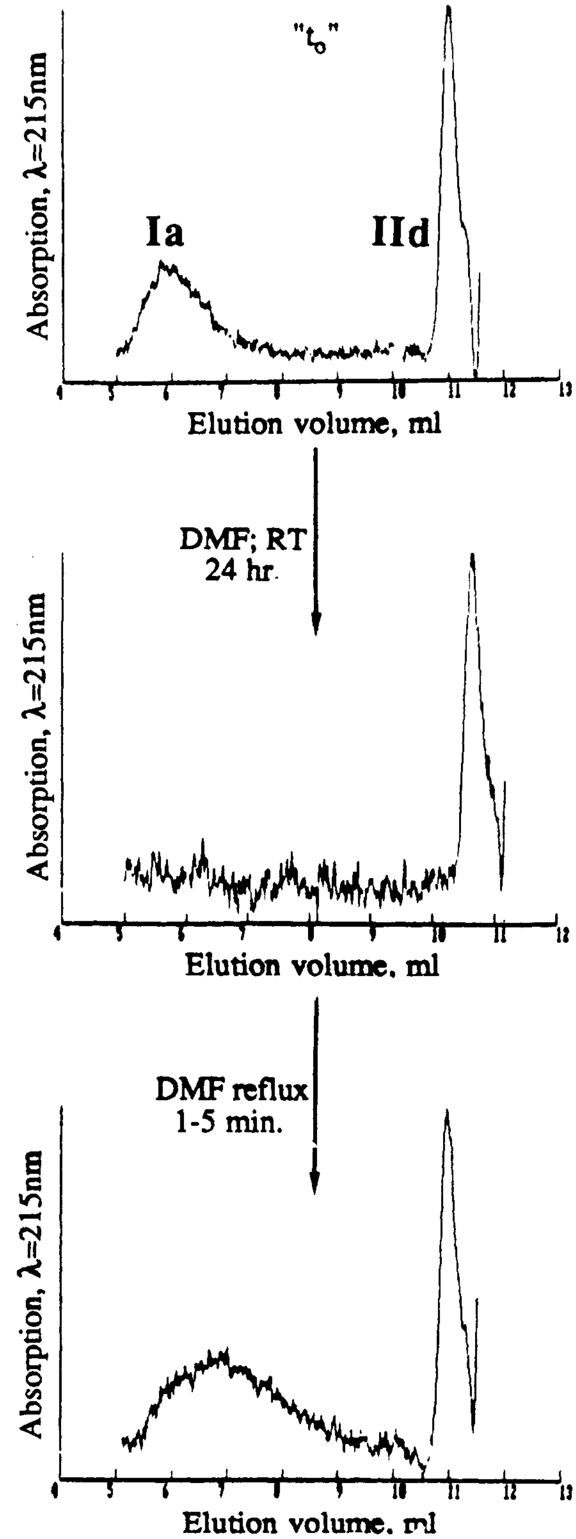


Figure 6. SEC traces of the reaction of Ia and 15% IId in DMF, taken at the points indicated.

Several reactions of both Ia and Ib with IId were then examined in the drybox. Both DMF and DMSO were used in order to find the ideal mixture to give reasonably fast gelation, fast reversibility (which would minimize degradation), and the most cycles (i.e., heating following by re-formation of gel).

Relative reactivities of II appeared to be the same in DMSO as observed for the DMF solutions. The reverse reactions in DMSO were run at 150–170 °C. DMSO reflux was avoided since the polymer begins to degrade at 160 °C. While 170 °C is a higher temperature than is reached in refluxing DMF, it was not expected to cause appreciable degradation of the polymer.

It was found that, apparently independent of temperature or the amount of IId used (2–15%), the DMSO solutions of Ia and Ib with IId run in the drybox failed to re-cross-link after four to five cycles. It was thought that perhaps at elevated temperatures the nucleophilic carbon of the sulfoxide could attack the azlactone ring, although earlier model studies in DMSO solution presented no evidence that this was occurring.[1,2] The DMSO used for cross-linking was fractionated in vacuo and stored inside the drybox, so it was assumed that water was not responsible for the observed failure to cycle. DMSO solutions were not investigated further.

A general observation for the DMF solutions with Ib was that the greater the amount of IId used, the faster gelation occurs. For solutions of 0.20 g/mL in Ib and 2–3% IId, gelation took about 18 h. At 15% IId, gelation took place within 1 h. All of the gels of I and IId in DMF formed solutions within 5 min after reaching DMF reflux. The cross-linking solutions made with the lower molecular weight polymer Ib formed solutions of significantly lower viscosity than the solutions with Ia, despite the higher concentration of Ib in DMF. Ib also survived more cycles before failure than Ia. In reactions run outside the drybox, this was particularly significant since a higher degree of failure occurred in air.

The differences in physical properties between the gels formed from Ia and Ib were noted only in a qualitative sense. The gels of Ib and IId while in DMF were stiffer than those with Ia and the same amount of IId, often forming hard plugs of material in the reaction vessels after gelation. The gels with Ia were more rubbery in nature when the solvent was present. Upon stripping off the DMF in vacuo (ambient temperature or slightly elevated temperature, 35 °C or less), the gels were not significantly different by observation. Both networks formed tough, flexible films. Although no physical properties were obtained, the materials felt much tougher than plastic food wrap or polyethylene garbage bags to the hand. Some yellowing was observed in the dry films, particularly when more than 5% IId was used.

Reactions were run outside the drybox with polymer and cross-linker that had been left in the air or in a stoppered bottle (no desiccant). Also, the solvent DMF used was HPLC grade and previously opened, such that atmospheric water was no doubt adsorbed. These conditions were used purposely—it was desirable to determine whether cycling of the cross-linking reactions would occur under conditions that were not rigorously dry. However, an argon blanket was used to prevent additional adventitious water from entering the reaction flasks, particularly during heating. When argon was not used during heating, all the reactions failed to cause gelation after only one or two cycles. The flasks under argon were periodically opened to permit qualitative evaluation of the gel, so the solutions were never allowed to become completely dry by blowing with argon.

The results of reactions run both inside and outside of the drybox are shown in Table II. The number of cycles in excess of 20 was not noted. The number of cycles recorded reflects cycles in the same solvent; i.e., the solvent was never stripped off to make films for any of these samples. This was done so that comparisons could be made between samples.

Note that polymer Ia failed to cycle more than a few times outside of the drybox until a high amount (15%) of IId was used. The solutions with 15% IId did, however, turn yellow to orange after only two to three cycles. Solutions with less cross-linker yellowed only slightly, and only after several more cycles. Polymer Ib fared much

Table II
Results of Thermal Cycling of the Cross-Linking Reaction of I with IId[a]

polymer	% Id	no. of cycles	in drybox?
Ia	2	6	Y
Ia	5	>20	Y
Ia	5	8	N
Ia	15[b]	>20	N
Ib	2	17	Y
Ib	5	>20	Y
Ib	5	15	N

[a] Reactions outside of the drybox were run under an argon blanket. [b] Yellowing of reaction mixtures containing ≥15% IId was observed in all experiments.

better outside the drybox. At only 5% IId, this network gives gelation over 15 cycles before failure. Even inside the drybox, Ib exhibited a better ability to cycle. For instance, Ia and 2% IId inside the drybox failed after only six cycles, whereas the analogous mixture using Ib went through 17 cycles before failure.

Thus the lower molecular weight and/or polydispersity of polymer Ib consistently provide more cycles before failure than doses Ia. There are several reasonable explanations for this observation. It may be a concentration effect, as the lower molecular weight polymer Ib was used to make solutions twice as concentrated as for Ia. Another possibility is that shorter polymer chains afford increased mobility in the system, and therefore the cross-linking reaction with Ib proceeds to a further extent at ambient temperatures. Finally, the polydispersities of the polymers themselves may contribute to the ability of the cross-linking reaction to take place. It can be seen in Figure 6 that the polydispersity of the polymer increased after only one cycle; as the polydispersity increases to infinite proportions, perhaps a network can no longer be formed. In any of these cases, polymer Ib would be better suited to undergo more cycles than Ia.

Conclusions

A truly thermoreversible, covalent network has been formed using this chemistry. This is recycling technology that could well be used for industrial applications. The networks so formed are qualitatively tough films after solvent removal, and several uses might be envisioned: plastic food wrapping or other packaging applications or grocery or garbage bags might be made from these films. This system represents the type of recycling technology that is becoming increasingly necessary, as the buildup of polymer wastes continues to be a problem.

Cross-linking forward reactions of polymer Ia with bisphenols II were carried out in THF solution and, with one exception, showed the expected trends of reactivity of II as evidenced by their relative abilities to gel the polymer at ambient temperature. The exception in this case was that bisphenol IId caused gelation of the polymer at a lower number of equivalents of IId than the other species II. The result was unexpected based on equilibration model studies which indicated that IId was less reactive than IIc in the forward reaction with azlactones. The observation in the cross-linking reaction was attributed to the greater flexibility of the molecule IId relative to other II.

The reverse (de-cross-linking) reaction was only observed in the case of IId in that the highest temperature examined was 170 °C. This temperature was low enough to avoid major degradation of the polymer backbone, as determined by TGA studies. High-boiling solvents (DMF and DMSO) were necessary to achieve the reverse reaction of the gels to re-form I and II. Bisphenol IId was successfully used to cycle the covalent network more than 20 times, in DMF solution, even outside the drybox (under an argon blanket) and using nonfractionated solvent. The reverse reaction in all cases occurred in 5 min or less once reflux (153 °C) was reached.

The cross-linking system using DMF as solvent and 0.20 g/mL of polymer Ib with IId as cross-linker was the most successful. The networks formed underwent several cycles of cross-linking and de-cross-linking. The use of polymer Ib allowed more cycles before failure; this was especially valuable when the reactions were run outside the drybox. Even under these nonrigorous conditions, the DMF solution of 0.20 g/mL of Ib with 5% IId underwent 15 cycles before failure. The solutions with 5% or less of IId also had less yellowing as the number of cycles increased; thus, using less cross-linker is favorable from the standpoint of yellowing as well as potential cost in an industrial use.

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