Diels−Alder Reactions with Novel Polymeric Dienes and Dienophiles: Synthesis of Reversibly Cross-Linked Elastomers

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ABSTRACT: Novel highly flexible copolymers bearing dienic or dienophilic moieties were prepared by either free radical copolymerization of hexyl acrylate and 2-furfuryl methacrylate or the chemical modification of siloxane copolymers with pendant primary propylamino functions. In addition, maleimides were synthesized from oligoether bis(amine)s and from the amino pendant groups of the polysiloxane. Diels−Alder reactions between these copolymers and difunctional complementary coupling agents produced cross-linked elastomers in high yields. The thermal reversible character of these networks was confirmed by applying retro-Diels−Alder reactions in the presence of appropriate trapping reagents which restored the initial linear polymers quantitatively.

Introduction

The Diels−Alder reaction generally provides simple, efficient, and clean procedures to generate new bonds by inter- or intramolecular coupling and represents one of the most useful synthetic methods in organic chemistry.[1,2] In this [4 + 2] reaction, a dienophile adds typically to a conjugated diene to give a cyclic product called an adduct. One interesting feature of this reaction is its thermal reversibility, which implies that its equilibrium can be easily displaced toward the reagents by heating (retro-Diels−Alder).

The furan ring is one of the most important heterocycles used as the diene in Diels−Alder reactions.[2,3] Interest in exploiting the Diels−Alder reaction in the context of furan chemistry is clearly shown by (i) the renewable character of these heterocyclic compounds (furfural is an industrial commodity obtained from a wide variety of agricultural residues) and (ii) the pronounced dienic nature of the furan ring which makes it particularly suitable in terms of kinetics and yields. In recent years, the main research topic of our laboratory has been the application of furan monomers and furan chemistry to macromolecular synthesis.[4] These investigations have required the synthesis of new furan monomers and the study of their homo- and copolymerizations with classical monomers, which give rise to original macromolecular structures bearing furan moieties in the main chain or as pendant groups.[4]

In a Diels−Alder reaction, the dienophile counterpart must contain a double or triple bond. Among the large variety of dienophiles, maleimides are among the most commonly used reagents because of their high reactivity.[5,6] The electron-attracting substituents attached to the double bond in maleimides promote the Diels−Alder reaction with furan compounds under smooth reaction conditions.

In macromolecular chemistry, this reaction has been used as a polycondensation process between difuran and bis(maleimide) monomers to obtain, for example, polyimide resins[7−9] and even optically active materials.[10] The same approach was followed when single AB-type monomers were employed.[11,12] A recent addition to this field is the synthesis of dendrons based on the furan−maleimide adducts.[13] The Diels−Alder reaction has been also employed as a useful technique to induce the cross-linking of various polymer structures by inter-macromolecular couplings with a difunctional complementary reagent, viz. furan copolymers plus bis(maleimide)s or polymers bearing maleimide moieties plus difurans.[14−18] Among these studies, only one thoroughly investigated the thermally induced de-cross-linking by calling upon the addition of an excess of a furan derivative to trap the liberated maleimide functions.[15] It is indeed this reversibility which constitutes, to our mind, the most interesting aspect of these studies, because it provides a promising perspective in terms of the possibility of recycling gelled materials by reverting them to their thermoplastic precursors. In particular, elastomeric materials, such as those utilized in the manufacture of tires, are a major concern in this context, given the vast amounts of scrap that accumulates because of the irreversible nature of vulcanized rubber. All the papers quoted above[14−18] dealt with polymers with glass transition temperatures well above room temperature and were therefore not related to elastomeric properties.

The purpose of this investigation was therefore to synthesize new, thermally reversible, elastomeric networks via Diels−Alder and retro-Diels−Alder reactions. The general method followed here was based on the synthesis of low-T_g polymers incorporating furan or maleimide pendant groups, followed by their Diels−Alder cross-linking with an appropriate difunctional complementary reagent. The ensuing networks were then de-cross-linked by heating them in the presence of an excess of a suitable monofunctional Diels−Alder trap. Two synthetic approaches were studied, namely (i) the synthesis of polymeric dienes, i.e., polymers bearing pendant furan moieties, and the use of a bis(maleimide) as the cross-linking agent and (ii) the synthesis of polymeric dienophiles, i.e., polymers bearing pendant maleimide moieties, and the use of a difuran as the cross-linking agent.

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Experimental Section

Materials. *n*-Hexyl acrylate and 2-furfuryl methacrylate (Aldrich) were purified by washing them with a 10% aqueous NaOH solution to eliminate the inhibitor and by fractional distillation at reduced pressure. *O*,*O*′-Bis(2-aminopropyl) poly(ethylene glycol) of molecular weight 600 (Fluka) and all other reagents and solvents (Aldrich) were used as received. Two siloxane copolymers with aminopropyl functional groups (AMS-162 and 132 supplied by ABCR) with molecular weights of 4500 and 5000, respectively, were used as precursors for dienophilic macromolecules. The contents of amino groups were determined by titration with perchloric acid in dioxane. This standard potentiometric method[19] provided the number of moles of the amino group per gram of polymer, viz. 1.86×10^{-4} and 8.41×10^{-4}, respectively, which were correlated with the corresponding molecular weights and gave 2.2 ± 0.1 and 3.4 ± 0.1 primary amine groups/polymer chain, respectively.

Product Characterization. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on 300 or 200 MHz AC Bruker instruments. Infrared spectroscopy was conducted with a Perkin-Elmer Paragon-1000 FTIR spectrophotometer. The glass transition temperatures (T_g) of the various polymers were determined by differential scanning calorimetry using a Setaram DSC-92 thermal analysis system. The temperature program provided cooling and heating cycles between −140 to 200 °C with a heating rate of 10 °C/min. Polymer molecular weights were determined with a SF400 Applied Biosystems gel permeation chromatograph, provided with two Styragel H3 and H4 columns and ultraviolet (240 nm) and refractometry detectors. The solvent used was tetrahydrofuran flowing at 0.7 mL/min at room temperature, and the calibration was carried out with standard polystyrene samples.

Synthesis of Polymeric Dienes. Poly(hexyl acrylate-*co*-furfuryl methacrylate)s, 1. The copolymers with pendant furan rings were prepared by free-radical polymerization using the following typical procedure: *n*-Hexyl acrylate (14.7 mL, 0.097 mol) and 2-furfuryl methacrylate (0.464 mL, 3 mmol) were dissolved in toluene together with 0.07 g (0.4 mmol) of AIBN as initiator. The reaction was carried out under nitrogen at 80 °C for 8 h. The final products were precipitated in methanol and dried under vacuum to constant weight. FTIR (NaCl, cm^{-1}): 3056, 2957, 2931, 2859, 1734, 1165, 1064, 920, 817, 599. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 0.9 (s, 100H), 1.32 (s, 194H); 1.6 (s, 64H); 2.25 (s, 32H); 4.0 (s, 64H); 4.9 (m, 2H); 6.42, 6.38 (m, 2H); 7.44 (s, 1H). ^{13}C NMR [CD_2Cl_2; δ (ppm)]: 14.17, 22.92, 25.92, 31.89, 39.75, 41.84, 65.02, 110.7, 110.90, 143.49, 150.06, 175.2. Anal. Calcd: C, 69.06; H, 10.19; O, 20.75. Found: C, 69.02; H, 10.23; O, 19.99.

Synthesis of Oligomeric Maleimide Dienophile. α,ω-Poly(ethylene oxide)bis(2-propylmaleamic acid), 2. A 0.98 g (10 mmol) amount of maleic anhydride was dissolved in 10 mL of dioxan. The α,ω-poly(ethene oxide)bis(2-propylamine) (3 mL, 5 mmol) was then added dropwise to this solution. The mixture was left at 80 °C for 1 h, after which the reaction medium was cooled, diluted with 500 mL of hexane, and then left refrigerated overnight. The product was finally filtered out, washed with hexane, and vacuum-dried to afford the corresponding maleamic acid as a yellow viscous liquid in 85% yield, $T_g = -49$ °C. FTIR (NaCl, cm^{-1}): 3509, 3268, 3070, 1717, 1632, 2871, 1574, 1353, 1113. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 1.2, 1.22, 1.24 (m, 12 H); 3.58, 3.62 (m, 52H); 6.21, 6.25, 6.46 (dd, 4 H); 4.15 (s, NH 2H); 8.10(s, OH, 2H). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 14.92, 16.41, 16.76, 46.73, 46.99, 69.79, 70.01, 71.21, 73.13, 75.04, 132.24, 135.35, 165.57, 169.19. Anal. Calcd: C, 55.25; H, 8.35; N, 2.99; O, 33.41. Found: C, 53.45; H, 8.23; N, 3.28; O, 35.16.

α,ω-(Poly(ethylene oxide)bis(2-propylmaleamide), 3. The maleamic acid **2** (3.5 g, 4.4 mmol) was dissolved in a mixture of 2.4 mL (15 mmol) of triethylamine and 15 mL of acetone. The resulting solution was heated at 60 °C before adding acetic anhydride (1.24 mL, 18 mmol) dropwise. The reaction mixture was then refluxed for 20 h, cooled, dissolved in an excess of methylene chloride, and washed with a saturated solution of sodium bicarbonate. The organic phase was washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was dried under high vacuum to afford the corresponding maleimide as a brown viscous liquid in 65% yield, $T_g = -43$ °C. FTIR (NaCl, cm^{-1}): 3089, 2870, 1708, 1634, 1573, 1375, 1348, 1109, 695. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 0.99, 1.28, 1.31 (m, 12H); 3.31, 3.58, 3.36 (m, 48H); 3.80 (m, 2H); 4.29 (m, 2H); 6.63 (s, 4H). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 15.02, 16.98, 46.19, 46.75, 69.23, 71.24, 73.17, 75.04, 133.78, 170.86. Anal. Calcd: C, 57.46; H, 8.24; N, 3.12; O, 31.18. Found: C, 55.51; H, 8.20; N, 3.44; O, 32.93.

Synthesis of Polymeric Dienophiles. The following synthesis describes the preparation of the copolymer with the highest content in maleimide functions: 10 g (0.084 mol of amino groups) of AMS-162 was added to 8.24 g (0.084 mol) of acetic anhydride in 50 mL of toluene and the ensuing solution heated at 80 °C overnight. The solvent was then removed to isolate the copolymer containing maleamic acid functionalities. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 0.09 (s, 96H); 0.57 (m, 2H); 1.67 (m, 2H); 3.35 (m, 2H); 6.28 (d, $J = 19.02$ Hz, 2H). FTIR (NaCl, cm^{-1}): 3258, 2962, 2904, 1709, 1631, 1565, 1548, 1260, 1090, 1019, 798. This modified copolymer (0.084 mol) was dissolved in 50 mL of methyl ethyl ketone, and then 11.7 mL (0.084 mol) of triethylamine and 7.9 mL (0.084 mol) of acetic anhydride were slowly added. The reaction was extended for 72 h at 40 °C, after which the solvent and the condensation water were eliminated under high vacuum. The resulting viscous liquid (**4b**) was recovered in 98% yield, $T_g = -112$ °C. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 0.08 (s, 115H); 0.48 (m, 2H); 1.61 (m, 2H); 3.46 (t, 2H); 6.66 (s, 2H). FTIR (NaCl, cm^{-1}): 2962, 1804, 1719, 1690, 1260, 1090, 1019, 798. The corresponding copolymer **4a** from AMS-132 was prepared likewise.

Synthesis of the Difuran Compound. Bis(2-methoxyfuran)dimethylsilane, 5. This bis-dienic compound was prepared by nucleophilic substitution of an alcohol with a dialkylsilyl dihalide.[10] Its FTIR spectrum was identical to that previously reported,[10] and its NMR spectra, not previously reported, gave the following. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 0.15 (s, 6H); 4.65 (s, 4H); 6.27 (t, 2H); 6.35 (d, 2H); 7.40 (s, 2H). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 57.00, 107.85, 110.26, 142.31, 153.51.

Model Diels-Alder Reactions. To assess the feasibility of the cross-linking reactions, model Diels−Alder systems were first studied using monofunctional counterparts.

(a) Model Adduct 6. A 0.7 g amount of 2-furfuryl acetate (5.2 mmol) was added to a solution of dienophile **3** (1 g, 1.3 mmol) in 4 mL of methylene chloride. The reaction mixture was stirred at room temperature for 1 day. The final product was purified by vacuum distillation and gave 62% of a viscous liquid, $T_g = -56$ °C. FTIR (NaCl, cm^{-1}): 2873, 1746, 1702, 1371, 1228, 1106, 955, 711. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 1.28, 1.17, 1.07 (m, 12H); 2.09 (s, 6H); 2.85 (1H); 2.92 (1H); 3.58 (m, 48H); 3.81 (2H); 3.83 (2H); 4.30 (m, 2H); 4.77−4.32 (dd, 2H); 5.26, 5.2 (2H); 6.29−6.63 (m, 4H).

(b) Model Adduct 7. A 0.7733 g (3 mmol) amount of **5** was added to 0.9389 g (6 mmol) of *N*-butylmaleimide in 10 mL of methylene chloride. The reaction was carried out during 16 h at room temperature. The solvent was vacuum eliminated, and the adduct **7** was obtained as an oily liquid in 89% yield. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 0.17 (m, 6H); 0.89 (t, 6H); 1.18−1.56 (m, 8H); 2.80−2.96 (m, 4H); 3.43 (t, 4H); 4.01−4.42 (m, 4H); 5.18, 5.25 (dd, 2H); 6.25−6.58 (dd, 4H). FTIR (NaCl, cm^{-1}): 3457, 2960, 2874, 1770, 1694, 1440, 1403, 1371, 1344, 1288, 1261, 1192, 1140, 1036, 981, 925, 886, 845, 805, 648, 609, 560.

Cross-Linking via the Diels−Alder Reaction. (a) Preparation of Network 8. A 2 g amount of **1d** (0.4 mmol) was dissolved in 6 mL of methylene chloride. After addition of 0.29 g of **3** (0.2 mmol), the reaction was stirred for 3 days at room temperature. The ensuing gel was purified by Soxhlet extraction with methylene chloride for 12 h. The final products was vacuum-dried giving 82% of insoluble material, $T_g = -63$ °C. FTIR (NaCl, cm^{-1}): 2955, 2918, 1731, 1715, 1154, 726.

(b) Preparation of Network 9. A 0.1899 g (0.75 mmol) amount of **5** was added to 1.7868 g (1.5 mmol) of **4b** in 15 mL of methylene chloride. The reaction mixture was stirred at room temperature for 3 days after which the solvent was eliminated and the gelled product purified by Soxhlet extrac-

Table 1. Characterization of Copolymers 1 with Pendant Furan Moieties

copolymer	FMA/HA molar feed	mol % of furan units (^{1}H NMR)	yield (%)	M_n	M_w/M_n	T_g (°C)
1a	30/70	31.7	62	13 000	2.4	−29
1b	10/90	10.9	65	14 500	2.3	−57
1c	5/95	5.4	66	25 000	2.2	−70
1d	3/97	3.1	70	33 500	2.1	−78

tion for 20 h using the same solvent. After drying, the insoluble fraction constituted 80% of the starting reagents, $T_g = -111$ °C. FTIR (NaCl, cm^{-1}): 2960, 1790, 1720, 1406, 1260, 1090−1000, 800.

Retro-Diels−Alder Reactions. (a) Model Adduct 7. A 0.8658 g (5 mmol) amount of *N*-phenylmaleimide was added to 1.3 g (2.47 mmol) of adduct **7** in 10 mL of toluene. The system was refluxed for 8 h. Adduct **11** was recovered in 85% yield by high-vacuum distillation. ^{1}H NMR [acetone-d_6; δ (ppm)]: 0.13 (m, 6H); 3.12, 3.21 (dd, 4H); 3.38−3.78 (4H); 3.95−4.40 (m, 4H); 5.23, 5.31 (s, d, 2H); 6.53, 6.63 (d, 4H); 7.17−7.39 (m, 10H). FTIR (NaCl, cm^{-1}): 3462, 3100, 2960, 2872, 1915, 1875, 1820, 1707, 1593, 1445−1337, 1284, 1180, 1115, 1038, 917, 830, 697. The retro-Diels−Alder reaction of **6** was carried out likewise using 2-methylfuran as trap: the corresponding adduct **10** was recovered in 88% yield.

(b) De-Cross-Linking of 8. A 0.5 g amount of **8** was suspended in 5 mL of chlorobenzene in the presence of an excess of 2-methylfuran (1 mL). The ensuing suspension was heated at 80 °C for 12 h as the gel dissolved progressively. Both the copolymer **1d** and the corresponding bis-adduct **10** were recovered quantitatively by precipitating the former in an excess of methanol and, after filtration, by vacuum evaporating the solvents to obtain the latter. FTIR (NaCl, cm^{-1}): 3055, 2926, 2872, 1699, 1453, 1104, 735. ^{1}H NMR [CD_2Cl_2; δ (ppm)]: 1.28, 1.26, 0.9 (m, 12H); 1.66 (s, 6H); 2.6 (d, 1H); 2.9 (d, 1H); 3.85 (m, 2H); 4.0 (m, 2H); 4.3 (dd, 2H); 5.1 (m, 2H); 6.63−6.29 (m, 4H).

(c) De-Cross-Linking of 9. A 0.7288 g (5 mmol) amount of *N*-phenylmaleimide was added to 0.5 g of gel **9** in 15 mL of toluene. After 2 h of reflux, the suspended gel had gone into solution. The residual *N*-phenylmaleimide was eliminated by extraction, and adduct **11** was removed by high-vacuum distillation, leaving the original polymer **4b** as residue. The retro-Diels−Alder reaction was quantitative.

Results and Discussion

Synthesis of Polymeric Dienes and Dienophiles. (a) Diene Copolymers 1. *n*-Hexyl acrylate (HA) and 2-furfuryl methacrylate (FMA) were copolymerized using monomer molar feed ratios between 3 and 30 mol % of furan monomer (Table 1). The copolymers were recovered by precipitation in methanol, and the corresponding yields are given in Table 1. Figure 1 gives a typical FTIR spectrum which exhibits, besides the typical absorptions of the acrylic ester group at 1734 and 1165 cm^{-1}, peaks at 3056, 1064, 920, 817, and 599 cm^{-1} corresponding to the furan ring, as well as the absence of an absorption for the C=C moiety around 1630 cm^{-1}, which is present in the spectra of both monomers. The compositions of the copolymers were determined from their ^{1}H NMR spectra, using the integration ratio of the peaks at 4.0 and 4.9 ppm arising from the acrylic CH_2 protons belonging to the aliphatic and furan monomer units, respectively. Figure 2 shows a typical ^{1}H NMR spectrum of a copolymer with the corresponding assignments. As shown in Table 1, the contents of FMA units in all copolymers were close to the corresponding feed compositions, suggesting that the reactivity of both monomers is roughly the same, as one would have expected from a pair of acrylic comonomers. Similar results were reported for the copolymerization of FMA with hydroxyethyl methacrylate.[20] The T_g of these copolymers (Table 1) ranged from −78 to −30 °C as a function of increasing furan unit content. The GPC tracings indicated that the M_n of the copolymers decreased and the molecular weight distribution widened (Table 1) as the proportion of the furan monomer increased. This is consistent with the occurrence of minor transfer reactions involving the capture of free radicals by the heterocycle.[4] These copolymers represent an original type of acrylic material in which the HA units ensure the elastomeric properties (low T_g brought about by the long aliphatic side chains), while the FMA units provide the pendant furan rings to be used as dienes in the subsequent Diels−Alder reactions.

(b) Bis(dienophile) 3. The synthesis of **3**, to be used for the cross-linking of polymeric dienes **1**, was performed in two steps, according to a modification of a reported method.[11] It was prepared from its oligoether diamine precursor by the reaction with maleic anhydride, which generated the intermediate maleamic acid whose subsequent dehydration with acetic anhydride and triethylamine gave **3** in 65% yield. The elemental analysis suggested that the expected bis(maleimide) had indeed been formed. The FTIR and ^{1}H and ^{13}C NMR spectra confirmed this conclusion. A comparison between the FTIR spectra of **2** and **3** showed the disappearance of the OH and NH peaks at 3509 and 3268 cm^{-1}, as well as the appearance of a single sharp peak for carbonyl groups at 1708 cm^{-1} instead of the double

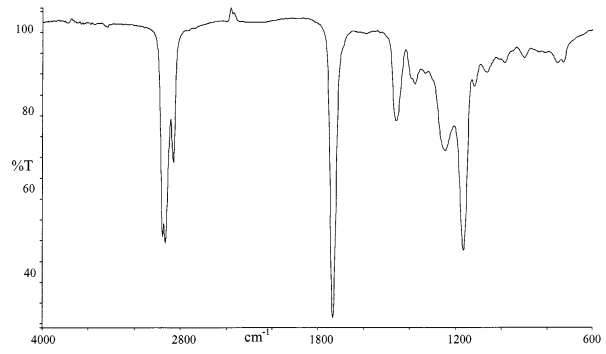


Figure 1. FTIR spectrum (NaCl plates) of copolymer **1d**.

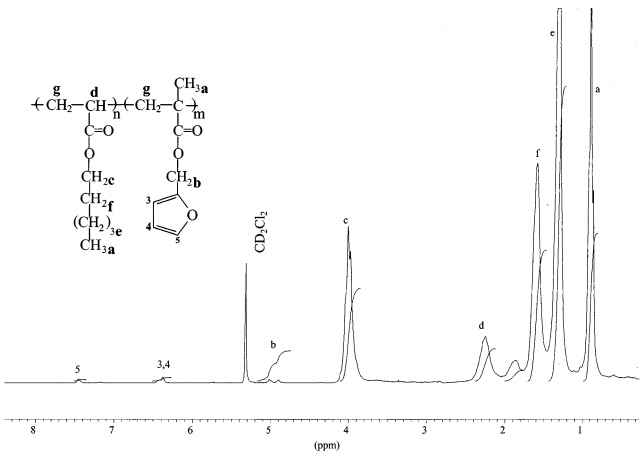


Figure 2. ^{1}H NMR spectrum of copolymer **1d** in CD_2Cl_2.

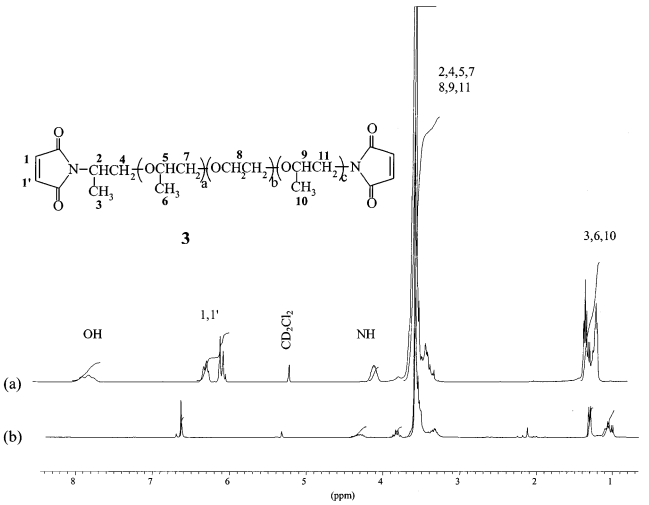


Figure 3. ^{1}H NMR spectra of (a) bis(maleamic acid) **2** and (b) bis(maleimide) **3** in CD_2Cl_2.

peak arising from the COOH and the CONH of **2**, demonstrating that the cyclization had taken place. Similar changes, illustrated by different ^{1}H NMR features related to these compounds, are shown in Figure 3. The two multiplets at 6.25 and 6.46 ppm for the protons attached to the C═C moiety in compound **2** become one singlet at 6.63 ppm for **3**. In the ^{13}C NMR spectrum of **3**, a single peak for carbonyl was observed at 170 ppm, instead of two different signals at 165 and 169 ppm for **2**. This bis(maleimide), as distinct from the common homologues used in polymer synthesis, is remarkably flexible because of its central oligoether segment, as reflected by its T_g of −43 °C.

(c) Polymeric Dienophile 4. Siloxane copolymers containing pendant propylamine chains were selected to prepare polymeric dienophiles using the same two-step method for the synthesis of the corresponding maleimide moieties. However, because of the macromolecular character of this system, reaction times longer than those used for small molecules were necessary to achieve complete conversion. The FTIR spectrum in Figure 4 shows the differences among the initial copolymer ($M_n \cong 5500$), the intermediate maleamic acid (appearance of peaks due to OH, NH, and carbonyl groups), and the final product **4** bearing maleimide units, with the same specific changes already discussed above for **2** and **3**. The expected structure was confirmed by comparison of the three corresponding ^{1}H NMR spectra, which exhibited, in addition to the common signals for the CH_3Si and the propyl chain protons, two peaks at 6.25 and 6.31 ppm for the maleamic acid structure compared and a single signal at 6.66 ppm in the case of the cyclized product **4**. The T_g's of the three polymers were similar at −112 ± 1 °C, suggesting that, given the very low degree of substitution, the dominant feature related to segmental motion arose from the PDMS chains. The chemical modification of these siloxane copolymers allowed the synthesis by an improved method of dienophilic polymers with the desired characteristics.

Model Diels-Alder Reactions. Two model adducts **6** and **7** were obtained from the reaction of 2-furfuryl acetate with **3** and of **5** with *N*-*n*-butylmaleimide (synthesized according to a published procedure[21]), respectively. Schemes 1 and 2 illustrate the reactions involved and the structures of ensuing **6** and **7**. FTIR analysis suggested the formation of both expected products. The structures of the model adducts were then established by ^{1}H NMR spectroscopy. In both cases, the key resonances occurred essentially at the same chemical shifts; thus, the peak of the proton at C5 of the furan ring at 7.4 ppm disappeared completely and new signals revealing the formation of the adduct were detected. Figure 5 shows the spectrum of **7** with the methyl protons attached to silicon at 0.17 ppm, the CH_3 and CH_2 protons of the butyl chain at 0.89, 1.28, 1.50, and 3.43 ppm, respectively, and the CH_2–O−Si protons at 4.01−4.42 ppm. The additional peaks assigned to the adduct were at 2.82 and 2.96 ppm for the H5 and H6 protons of the fused rings, as well as the bridgehead H7 proton signals at 5.18 and 5.25 ppm, whose relative integrals determine the ratio of *exo* and *endo* stereoisomers. The H8 and H9 protons of the double bond resonated at 6.25−6.58 ppm. As for the coupling of **3** with 2-furfuryl acetate, an inspection of the ^{1}H NMR

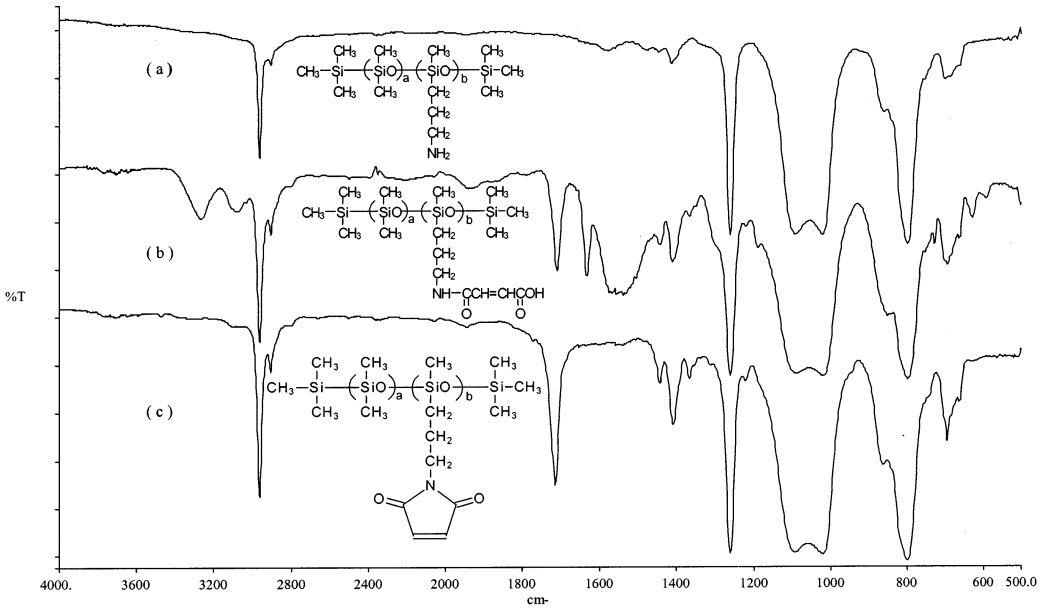
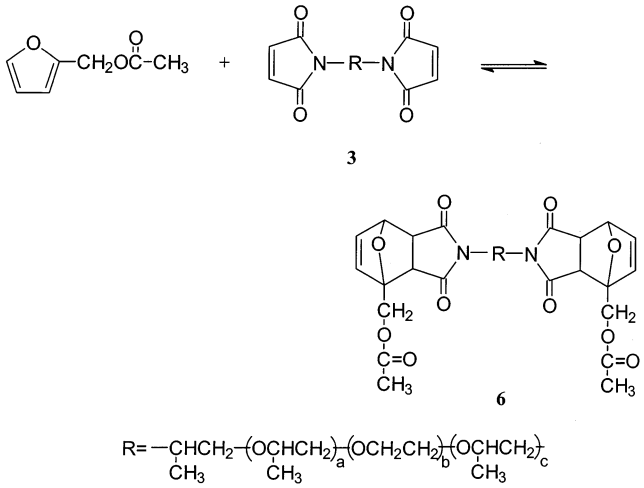
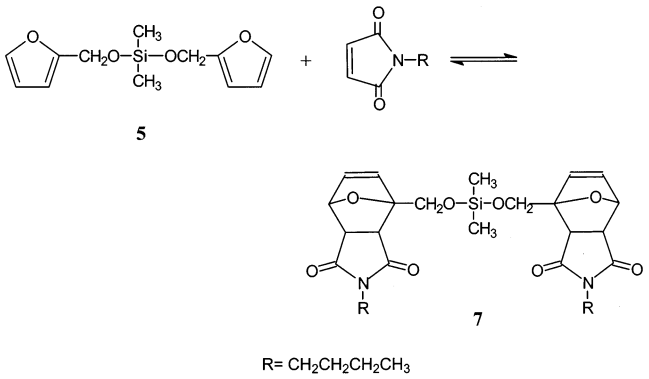


Figure 4. FTIR spectra (NaCl plates) of siloxane copolymers with (a) amino functionalities, (b) maleamic acid functionalities, and (c) maleimide functionalities.

Scheme 1. Diels−Alder Model Reaction between 2-Furfuryl Acetate and 3



Scheme 2. Diels−Alder Model Reaction between 5 and *N-n*-Butylmaleimide



spectrum of the product provided the same type of positive evidence as discussed above.

The retro-Diels−Alder reactions of **6** and **7** were also studied, using the conditions described in the Experimental Section. In both cases, the adducts reverted to the corresponding reagents in quantitative yields, as shown by the absence of the characteristic spectroscopic signals attributed to the adducts and the formation of the corresponding adducts of **3** with 2-methylfuran and of **5** with *N*-phenylmaleimide (see below). No side products were detected indicating that the conditions selected were appropriate for both model and polymer retro-Diels−Alder reactions.

Thus, although both model reactions gave good yields of adducts, when carried out under mild conditions, the reverse reactions reached completion with the procedure adopted here. Moreover, sound spectroscopic criteria were acquired for future structural assessments of the various adducts formed in all these operations.

Cross-Linking via the Diels−Alder Reaction. Schemes 3 and 4 summarize the mechanisms involved in each cross-linking step. The procedure in Scheme 3 was applied to all the copolymers **1** shown in Table 1 and obtained in each instance a high yield of cross-linked product. However, more attention was devoted to **1d**, containing 3 mol % of pendant furan groups, because, in addition of its lower T_g, this copolymer should generate the typical content of cross-linking sites found in common vulcanized elastomers. The use of the highly flexible bis(maleimide) **3** as the cross-linking agent also guaranteed the synthesis of a low-T_g network. Indeed, the T_g's of the four cross-linked products were only 10−15 °C higher than those of the corresponding linear copolymer precursors.

The reaction of copolymers **4** with **5** following Scheme 4, when **4a** was tested, i.e., the copolymer with the lower maleimide content, produced an entirely soluble material. Its ^{1}H NMR spectrum showed the typical signals of the corresponding Diels−Alder adducts, confirming that the reaction had taken place, but suggesting that the extent of intermolecular coupling had not been sufficient to give rise to a network. The same procedure applied to copolymer **4b**, richer in reactive moieties, was successful in producing the expected gel. The FTIR spectrum of this cross-linked polymer **9** confirmed the absence of absorption at frequencies characteristic of the furan ring (3148, 3120, 1504, and 737 cm^{-1}), as shown

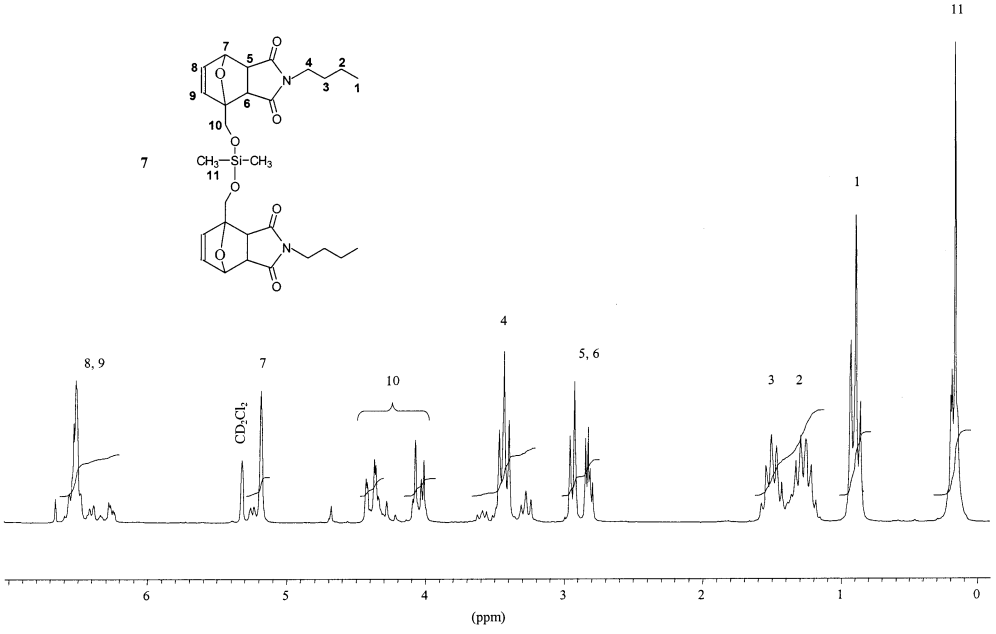
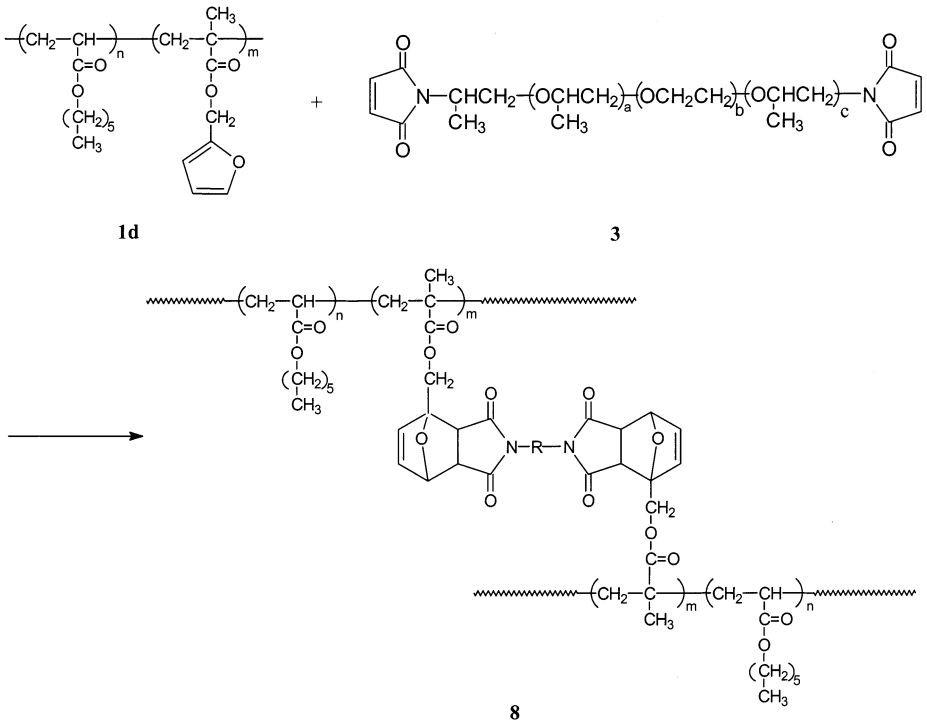


Figure 5. ^{1}H NMR spectrum of model adduct **7** in CD_2Cl_2.

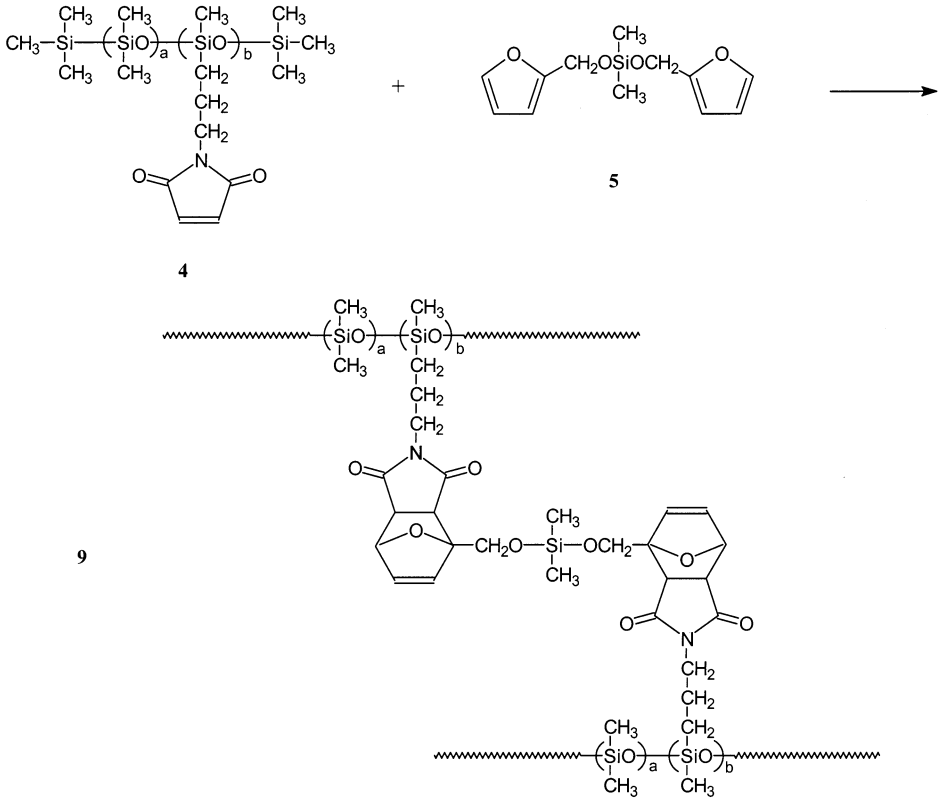
Scheme 3. Diels–Alder Cross-Linking Reaction of the Copolymers Bearing Pendant Furan Moieties 1 with Bis(maleimide) 3



1d **3**

8

Scheme 4. Cross-Linking Diels–Alder Reaction of Copolymers 4 with the Difuran Compound 5 as the Cross-Linking Agent



4 **5**

9

in Figure 6. Its T_g was −111 °C, i.e., very close to that of its linear precursor **4b**.

In both approaches, all initial compounds were liquids at room temperature, albeit of varying viscosity, whereas the ensuing Diels–Alder gellike polyadducts were rubbery solids. The amount of soluble fraction recovered from the extraction procedures varied as a function of the actual molar content of reactive functions appended to the copolymers and ranged from 100% for **4a** to about 20% for **1d** and to only 2–4% with the others. These fractions were analyzed by ^{1}H NMR spectroscopy and showed that the characteristic peaks of Diels–Alder adducts were near 5.2 ppm and from 6.24 to 6.65 ppm. Thus, the structures involved corresponded to poly-

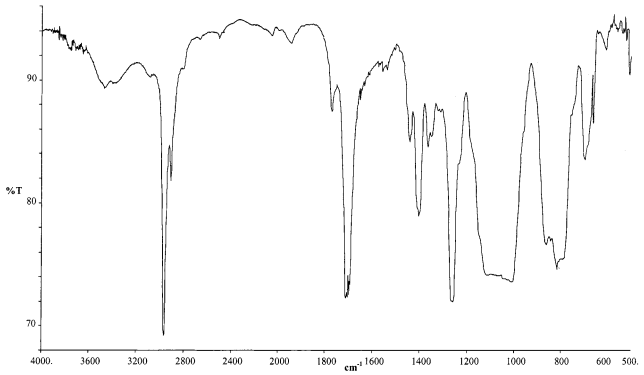
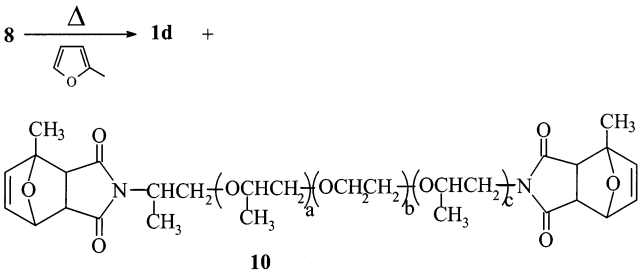
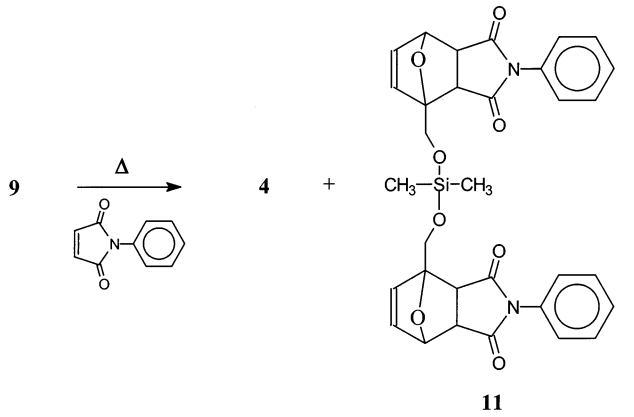


Figure 6. FTIR spectrum of a thin film of cross-linked polymer **9** between two NaCl plates.

Scheme 5. Retro-Diels–Alder Reaction of Cross-Linked Copolymer 8 in the Presence of an Excess of 2-Methylfuran



Scheme 6. Retro-Diels–Alder Reaction of Cross-Linked Copolymer 9 in the Presence of an Excess of *N*-Phenylmaleimide



adducts which had not yet reached a continuous network architecture but were already branched and/or bridged macromolecules.

De-Cross-Linking via the Retro-Diels–Alder Reaction. The thermal reversibility of this reaction was proved by cleaving the poly-adducts at high temperature and by subsequently trapping the cross-linking agent to avoid regenerating the networks following Schemes 5 and 6. The completely solubilized copolymers were recovered together with the Diels–Alder adducts **10** and **11**. The FTIR and ^{1}H NMR spectra of the copolymers were identical to those of the original **1d** and **4**, respectively, thus proving that the retro-Diels–Alder reactions had occurred in quantitative yields. Figure 7 shows the ^{1}H NMR of **10**, which displayed the features of the expected Diels–Alder adduct, namely the H2 and H3 signals at 6.29–6.63 ppm, the H4 signal at 5.1 ppm, and resonances at 3.8–4.0 and 2.6–2.9 ppm of the *endo* and *exo* H5 and H6 protons, respectively. Moreover, the

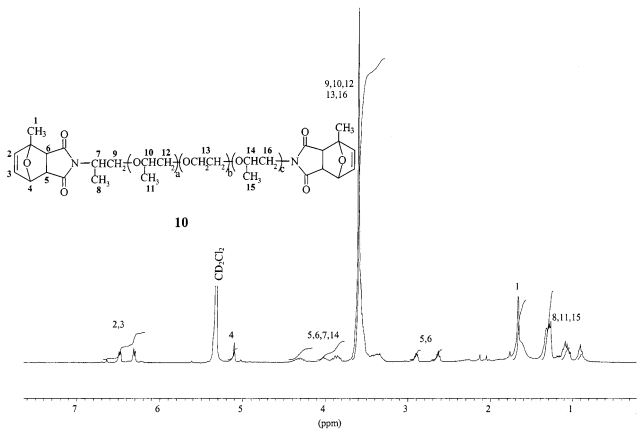


Figure 7. ^{1}H NMR spectrum of adduct **10** in CD_2Cl_2.

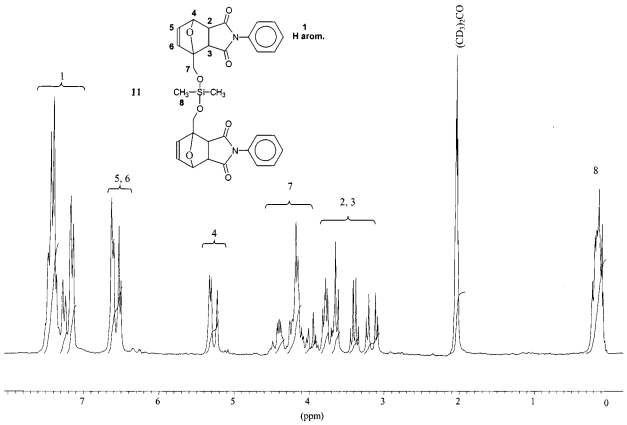


Figure 8. ^{1}H NMR spectrum of adduct **11** in $(CD_3)_2CO$.

GPC tracings of the recovered copolymers were identical to those of the original samples, suggesting the absence of degradation reactions during the retro-Diels–Alder reactions.

The expected chemical shifts were also found in the ^{1}H NMR spectrum of adduct **11** (Figure 8), which was practically identical to that of model adduct **7** (Figure 5), except for the replacement of the peaks of the aliphatic protons of the *n*-butyl group by the aromatic counterparts resonating between 7.17 and 7.39 ppm.

Conclusion

The strategy adopted in this study of the Diels–Alder cross-linking/de-cross-linking of elastomeric polymers, on the basis of the coupling–decoupling of furan + maleimide moieties, appears to be entirely satisfactory in terms of relative simplicity and efficiency. In particular, it applied successfully in both directions, i.e., with furan heterocycles or maleimide functions pendant to the copolymer chains and oligomeric bis(maleimide)s or small difuran molecules as coupling agents, respectively. Cross-linking took place effectively even with copolymers bearing a modest amount (3–5%) of reactive side groups. The de-cross-linking was ensured by heating the networks in the presence of an excess of complementary monofunctional reagent, used as a trap for the bifunctional molecule, released by the retro-Diels–Alder reaction.

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