Functionalization of coumarone-indene resins
I. Acetoacetylation

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Summary

A low molecular weight coumarone (or 2,3-benzofuran)-indene resin was converted to a β-ketoester functional material by Friedel-Crafts acylation with acetyl chloride, reduction to a secondary alcohol and reaction with t-butyl acetoacetate. Each reaction was essentially quantitative as shown by spectroscopy and elemental analysis. The final product proved to be crosslinkable at ambient or elevated temperature by the addition of multifunctional amines.

Introduction

Coumarone-indene resins are a well known, readily available class of resins that have a long history of use in the coating and printing ink fields (1-3). However, as newer types of synthetic resins became available, use of coumarone-indene resins declined (4). We believe that these resins could still be useful as base materials for the synthesis of new species with potential in value added applications. We have also been investigating the synthesis of polymers containing moieties capable of undergoing crosslinking at various temperatures (5-7). Specifically we have concentrated on the synthesis and evaluation of -ketoester functional polymers. Therefore, we decided to investigate the synthesis of such moieties starting with coumarone-indene resins. This paper summarizes some of the results we have obtained to date.

Experimental

All chemicals, including the coumarone-indene resins, used in this study were obtained from the Aldrich Chemical Company and were used as received. Nuclear magnetic resonance spectra were obtained at ambient temperature on $CDCl_3$ solutions of material with a Varian Gemini 300 FT NMR. Molecular weight measurements were made with a GPC equipped with a Waters 510 pump and 410 RI detector, two Polymer Labs 30 cm ultrastyragel columns and a 6 cm Polymer Labs guard column. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Acylation of Coumarone-Indene Resin

The resin was acylated by a published procedure (8,9). To a 500 ml flask equipped with a mechanical stirrer, reflux condenser, thermometer and pressure equalizing addition funnel were charged 41.34g (0.31 mol) of $AlCl_3$ followed by 100 ml of CS_2. To this well stirred mixture, 19.43g (0.25 mol) of acetyl chloride was added in three portions at approximately 10 minute intervals. There was a mild exotherm on addition of each aliquot of acetyl chloride (5-7°C temperature increase). After the addition of the acetyl chloride was complete, the polymer (20g), dissolved in 100 ml of CS_2, was added from the addition funnel over the course of 1 hour. After the addition of the polymer solution was complete, the reaction mixture was heated to the reflux point of CS_2. When the reflux point was reached a vigorous evolution of HCl commenced and a large mass of soft solid separated from the reaction mixture. After 30 minutes at reflux this solid mass redissolved. The reaction mixture was then stirred at reflux for 1 hour. The reaction mixture was cooled to 0 °C in an ice bath and H_2O (125 ml) was cautiously added from the addition funnel to destroy any unreacted $AlCl_3$. After the addition of H_2O was complete, the liquid layer was decanted and the remaining solid was washed with two 100 ml portions of acetone. The acetone was filtered to remove insoluble material and the modified polymer was obtained by addition of the acetone solution to CH_3OH. The polymer was purified by two reprecipitations from acetone solution into CH_3OH. Isolated yield = 22.9 g.

Reduction of Polymeric Ketone (10)

A 250 ml flask equipped as described above was charged with $NaBH_4$ (1.7 g), ethylene glycol dimethyl ether (60 ml) and isopropanol (15 ml). The polymeric ketone (28 g) was dissolved in 60 ml of ethylene glycol dimethyl ether and this solution was added to the flask from the addition funnel over the course of 45 minutes. After the addition of the polymer solution was complete the reaction mixture was stirred at ambient temperature for 1 hour and then at reflux for 1 hour. After cooling the reaction mixture to ambient temperature, 40 ml of 0.2M aqueous NaOH was added and this mixture was stirred for 1 hour at ambient temperature. The polymer was isolated by filtering the reaction mixture and adding the liquid to excess diethyl ether. The polymer was purified by reprecipitation from dioxane solution into diethyl ether. Yield = 26.1 g.

Synthesis of β-Ketoester (11)

A 250 ml flask equipped with a magnetic stirrer, Dean-Stark trap, reflux condenser and thermometer was charged with 8.0 g of the polyol obtained above dissolved in 100 ml of dioxane. t-Butyl acetoacetate (7.8 g) was added and the reaction mixture was heated to 103°C, at which point t-butanol began to distill at a steady rate. The reaction mixture was cooled and added to excess diethyl ether to precipitate the polymer. The polymer was purified by two reprecipitations from dioxane into diethyl ether. Yield = 10.4 g.

Film Crosslinking

The films were crosslinked by reaction with a diamine, 1,6-hexamethylene diamine. The crosslinks are a result of enamine formation, as shown in Scheme 1 (11,12).
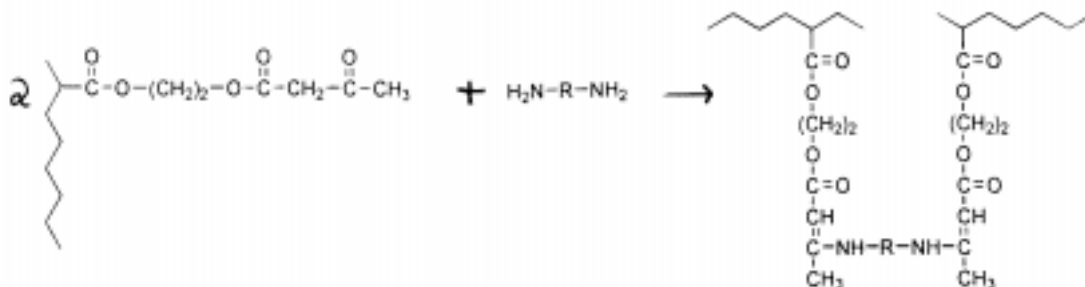
Scheme 1

Crosslinked films of the β-ketoester functional coumarone-indene resins were made as follows: 10 grams of polymer was dissolved in 10 g of methyl ethyl ketone. 1,6-hexamethylene diamine, 1.0 g premixed with 1.5g of methyl ethyl ketone was then added and the solution was stirred vigorously for 3-5 minutes. The solution was then drawn over glass or metal panels by using a #3 Bird bar. The dry film thicknesses were 0.03-0.05 mm. The films were cured either at ambient temperature or at elevated temperature by baking the panels at 130°C for varying lengths of time. Solvent resistance as a measure of cure, was assessed by rubbing the films with a methyl ethyl ketone saturated cloth using an AATCC Atlas Crockmeter. Degree of cure was also estimated by solvent extraction studies using tetrahydrofuran as the solvent. A weight quantity of film (from those cast on glass) was placed in 10 ml of tetrahydrofuran in a tightly sealed vial. The polymer film was kept in the tetrahydrofuran for seven days at ambient temperature. The vial contents were periodically agitated by vigorously shaking the vial. The polymer was removed from the vial and dried in vacuo at 30°C until a constant weight was obtained.

Results and Discussion

The [1]H-nmr spectra of the coumarone-indene resin at each stage of the modification are shown in Figures 1 and 2. The peak assignments are given in the Figures (13,14). Integration of the peaks shows that each reaction in the sequence is essentially quantitative; i.e. the isolated polymer has one functional group/coumarone-indene residue. Peak areas were measured via electronic integration and by computer simulation using deconvolution techniques as detailed in references 15 and 16. By comparing the areas of the aromatic proton resonances with the aliphatic resonances the extent of reaction (± 3%) could be calculated.

The degree of substitution is further confirmed by the elemental analysis results summarized in Table 1.

TABLE 1
Elemental Analysis

Polymer[a]	% C (Calc.)	% H (Calc.)	% O (Calc.)	% C (Found)	%H (Found)	%O (Found)
AcCI	81.63	6.03	12.34	81.64	6.22	12.14
RAcCI	80.61	7.20	12.19	80.34	7.00	12.56
AAcCI	72.55	6.36	21.09	72.91	6.25	20.84

a. AcCI = Acetylated coumarone-indene resin; RAcCI = reduced acetylated coumarone-indene resin; AAcCI = acetoacetylated coumarone-indene resin.

Elemental analysis results on the starting coumarone-indene resins indicated a coumarone/indene ratio of 2/7. The calculated results presented in Table 1 are based on this ratio.

The effect of modification on resin molecular weight is summarized in Table 2.

TABLE 2
Molecular Weight

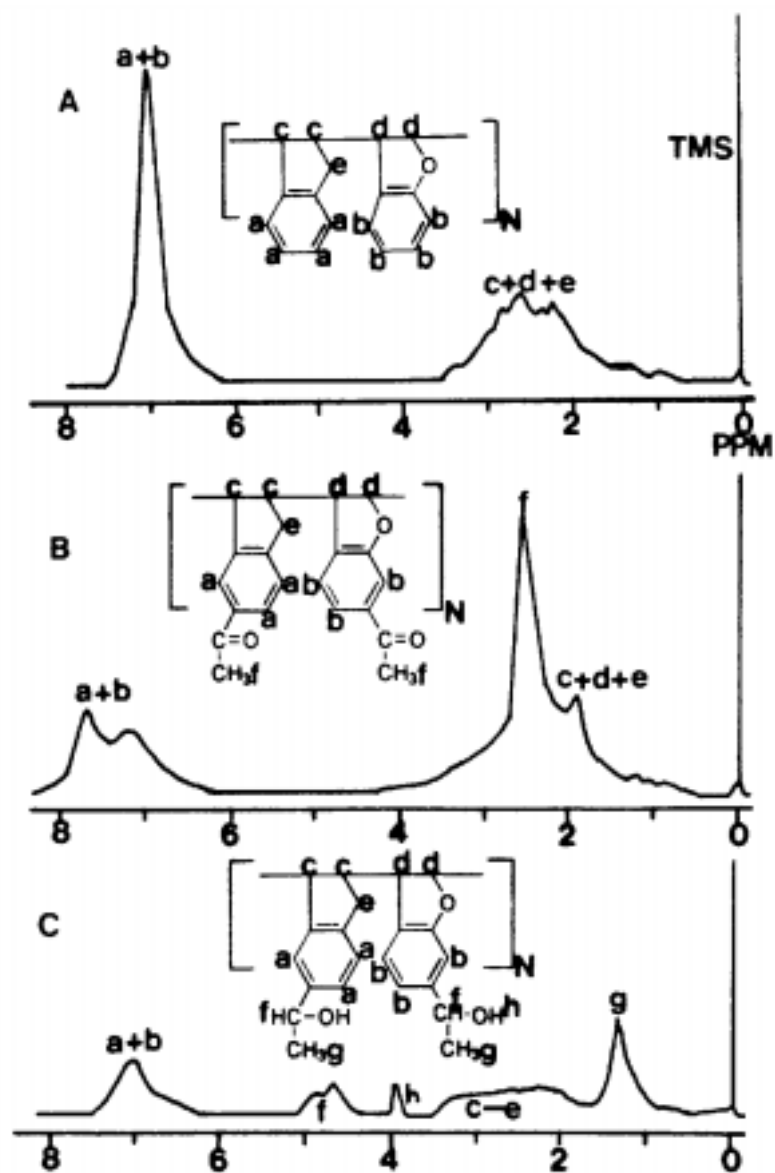| Polymer	M_n (Found)	M_w (Found)	M_n (Calc.)	M_w (Calc.)
CI[a]	1150	2200	–	–
AcCI	1600	2700	1430	2850
RAcCI	1620	2860	1500	2920
AAcCI	1800	3000	1710	3300

a. CI = Coumarone-indene starting resin.

Figure 1

300 MHz ^{1}H-NMR Spectra: A) Polycoumarone-indene resin;
B) Acetylated polycoumarone-idene resin;
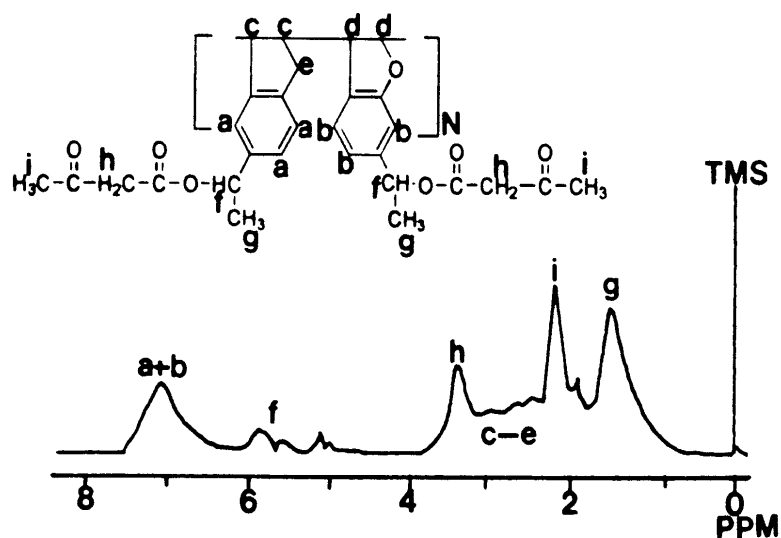C) Reduced acetylated polycoumarone-indene resin

Figure 2
Acetoacetylated Coumarone-Indene Resin

The molecular weights obtained are in good agreement with those expected for quantitative reaction given that a polystyrene calibration curve was used to obtain numerical values for the molecular weight. Examination of the coumarone-indene resin structure suggests that the solution behavior of such a resin might be expected to be somewhat different than that of polystyrene. The modified resins would be more different still so the found values of the molecular weights might reasonably be expected to be different than the calculated values.

The cure times and conditions as well as some of the properties obtained are summarized in Table 3.

The ketone double rubs are reported as the number of rubs required to break through the film to the substrate below. For the baked films, no damage to the films was observed after 200 double rubs, so no further rubbing was done. All the results reported in Table 3 were obtained from films cast on metal panels (Bonderite 1000). The results for glass substrates are similar. A control film was evaluated for the baked films and the films cured at ambient temperature. The control in each case was the acetoacetylated resin without the diamine crosslinker added.

TABLE 3
Film Cure Results

Cure Temp. (°C)	Cure Time (Min.)	Methyl Ethyl Ketone Double Rubs	Pencil Hardness
130	30	200+	8H
130	60	200+	8H
130	90	200+	8H
22	2880	160	6H

The baked film control had 15 methyl ethyl ketone double rubs, while the ambient film obtained 11 methyl ethyl ketone double rubs. Both controls had 2H pencil hardness (8H = highest pencil hardness rating) ratings. The results of the extraction experiments are presented in Table 4.

TABLE 4
Extraction Experiments

Cure Time (Min.)	Cure Temp. (°C)	Wt % THF Insoluble Material
30	130	95.8
60	130	96.5
90	130	100.0
2880	22	87.2

These results show that the films obtained are heavily crosslinked even at ambient temperature. This high crosslink density is expected given the low molecular weight and high functionality of these resins. Such crosslink density also results in brittleness (the films are very hard). The impact resistance is very low and the films crack easily.

Conclusions

We have shown that a crosslinkable resin can be readily obtained from a relatively inexpensive 'nonfunctional' resin through chemical modification. The modification reactions give high yields of quantitatively functionalized resins as was shown by [1]H-nmr and elemental analysis. Films from the acetoacetylated resin could be crosslinked at ambient or elevated temperatures. That the films were heavily crosslinked as shown by solvent resistance and extraction experiments. The films were very hard and quite brittle, cracking easily.

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