Synthesis, Characterization and Polymerization of Acetylacetate, Acetylacetamide or Acetylacetanilide Substituted Cyclic Imino Ethers, New Metal Chelating Monomers and Polymers.

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SUMMARY: New cyclic imino ether monomers, functionalized with acetylacetoxy, acetylacetamide, or acetylacetanilide moieties are described for the first time.These monomers readily form metal complexes. Also, it is shown that these monomers may be cationically homo- or copolymerized with other cyclic imino ethers, to provide polymers having metal complexing ability. The monomers have potential applications in a wide variety of applications

Introduction

It is well known that cyclic imino ethers, i. e., oxazolines and oxazines, will undergo cationic, ring-opening polymerization$^{1-4)}$, as well as form 1-to-1 adducts with carboxylic acids, phenols, mercaptans, thiophenols and alkyl halides. Also, bisoxazolines or bisoxazines will undergo step-growth reaction or copolymerization with dicarboxylic acids$^{5,6)}$, dithiols$^{7)}$, phenolic resins$^{8-12)}$ and other functionalized materials, including coupling or chain extending polyesters$^{13)}$.

As part of a program to design new monomers and polymers for formulation of water-borne, ambient curable coatings and adhesives, we recently studied new aryl cyclic imino ether monomers having acrylate or methacrylate functionalitites $^{14,15)}$, which worked reasonably well for the application. While doing this sponsored work, we also observed the interest of our client in working with β-keto esters for ambient curable coatings development. It was clear that monomers having the β-keto ester group were also very useful for development of water-borne, ambient curable coatings and other materials $^{16-18)}$. One of the most useful monomers in this category is 2-((2-methyl-1-oxo-2-propenyl)oxy)ethyl 3-oxobutanoate, more commonly called 2-(acetoacetoxy)ethyl methacrylate (AAEM) by Eastman Chemical$^{19)}$. Further, it is also known that β-keto esters readily form metal complexes $^{20-23)}$, some of which are often highly colored and useful as catalysts in a variety of applications.

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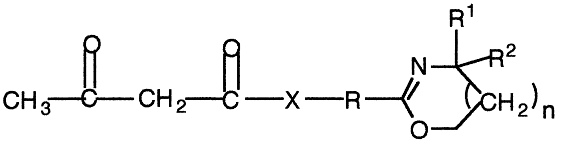
While reviewing the literature on the above two families of monomers, i. e., two types of functionalities, we became aware that no study had ever been carried out on monomers having both acetoacetoxy and cyclic imino ether type groups on the same molecule. Thus, we provide this preliminary report on studies we recently accomplished focusing on the synthesis, characterization, polymerization, and metal chelating properties of monomers having the generic compositions shown in structure 1. In structure 1, the X may be O, S, NH, NR, etc., while R may be a variety of alkyl and or aryl residues, including such things as a liquid crystalline moiety. The R^1 and R^2 may be such things as H or CH_3 residues and n = 0 or 1.



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It was our hypothesis that compositions having type 1 structures could have great utility in crosslinking reactions for coatings and adhesives development, as well as be useful for forming metal complexes, having applications in a number of areas. Also, these new monomers would open up a variety of studies due to being both unknown and having such high functionality. This partially explains why we started exploring monomers containing both the cyclic imino ether and acetylacetate, acetylacetamide, or acetylacetanilide type moieties on the same molecules. These heretofore unreported, highly functional monomers afford many opportunities to prepare other new monomers and polymers, as well as metal chelating materials.

Materials

The monomers and chemicals, 3- and 4-aminobenzonitrile, 2-aminoethanol and 3-aminopropanol, para-hydroxybenzonitrile, ethylene carbonate, methyl iodide, diketene, and methyl p-toluene-sulfonate, were used as received from Aldrich Chemical Co. The 2,2,6-trimethyl-1,3-dioxin-4-one, supplied by Wacker Chemical Co. [24)], was also used as received. The 2-ethyl- and 2-phenyloxazoline and anisole, received from commercial sources, were distilled prior to use.

Instrumentation

The NMR (^{1}H and ^{13}C) spectra were collected on a 400 MHz Bruker AM spectrometer, using deutrated chloroform as a solvent and TMS as an internal standard. FT-IR spectra were obtained on a MIDAC spectrophotometer. Mass spectra were recorded on a MAT-900 machine in the OSU Chemical Instruments Center. Viscosities were measured on a Brookfield Engineering Laboratories CAP 2000 cone and plate viscometer. Thermal analysis data was collected using TA Instruments 910 Differential Scanning Calorimeter, with scanning under N_2 at a rate of 10 °C.

Synthesis of Monomers

Synthesis of 2-(4-acetoacetanilide)oxazoline (1A). To a stirred solution of 2(4-aminophenyl)oxazoline $^{25)}$. 20.4 g (0.136 mol), and 280 ml of tetrahydrofuran (THF), contained in a 500 ml round bottom flask fitted with a reflux condenser and N_2 sparge tube, was added 10.8 ml (0.14 mol) of diketene in dropwise fashion, keeping the temperature at 0-5 °C. After 30 min, the temperature was allowed to rise to room temperature and the flask and contents allowed to sit for several hours. Evaporation of the solvent yielded a crude, solid product in essentially quantitative yield. Recrystallization from acetonitrile produced white, crystalline 1A having mp. 171-172 °C. Elemental analysis: Found: C=63.32; H= 5.76; N=11.27%; Theory: C= 63.41; H=5.69; N=11.38%. FT-IR (KBr, cm^{-1}) showed 1720 (CH_3COCH_2) 1668 (CH_2CONH), 1645 (CN) and 1604 (phenyl). ^{1}H NMR (ppm) showed δ 2.26 (s, 3H) 3.54 (s,2H) 3.99 (t,J=9.25 Hz, 2H), 4.38 (t,J=8.75 Hz, 2H), 7.58 (d, J=5.0 hz, 2H), 7.84 (d, J=5.0 Hz, 2H), and 9.52 (s, 1H). 13C-NMR (ppm) showed chemical shifts at δ 31.02, 50.05, 54.68, 67.55, 119.36, 123.45, 129.08, 140.39, 163.94, 164.25 and 204.65. cMass spectrometry showed m/z = 246.10 (calc. : 246.26).

The synthesis of 1A was repeated, using 2,2,6-trimethyl-1,3-dioxin-4-one (TDO)$^{24)}$ rather than diketene. A 250 ml three-neck, round bottom flask was fitted with a nitrogen gas inlet tube, magnetic stirrer, thermometer, and condenser. 2(4-Aminophenyl)oxazoline, 8.0g (54 mmol), was mixed with TDO, 8.0 ml (61 mmol), and 120 ml of xylene. The solution was heated at reflux, under a slow nitrogen stream, for 4 hrs. On cooling, the crude IA precipitated from solution.The 1 A was collected by suction filtration, washed with diethyl ether, and dried in a vacuum to obtain a slightly yellow, crystalline monomer in 83 % yield, having mp. 169-171 °C. FT-IR and ^{1}H-NMR confirmed the product to be the same as the previously prepared 1A.

Synthesis of 2-(3-acetoacetanilide)oxazoline (1B). Using the first described procedure for IA, 2(3-aminophenyl)oxazoline, prepared by the same method previously reported for 2(4-aminophenyl)oxazoline synthesis[25)] was treated with a slight excess of diketene to produce 1B monomer in 65 % yield, with the recrystallized waxy solid having mp. 77-78 °C. FT-IR (KBr, cm^{-1}) showed 1720 ($CH_3\mathit{CO}CH_2$), 1668 ($CH_2\mathit{CO}NH$), 1647 (C=N) and 1606 (phenyl). ^{1}H-NMR (ppm) showed δ 2.23 (s, 3H), 3.52 (s, 2H), 3.97 (t, J=10.0 Hz, 2H), 4.35 (t, J=11.25 Hz, 2H), 7.64 (m, 3H), 7.98 (s, 1H), 9.46 (s, 1H). ^{13}C-NMR (ppm) showed chemical shifts at δ 30.59, 50.37, 54.65, 67.64, 117.91, 123.08, 124.03, 126.39, 132.34, 137.82, 160.34, 164.34, and 204.46. Mass spectrometry showed m/z = 246.06 (calc.: 246.26).

Synthesis of 2(4-acetoacetanilide)oxazine (1C). Using the TDO method for 1A production, 2(4-aminophenyl)oxazine, prepared by a previously described procedure for 2(4-amino-phenyl)oxazoline synthesis [25)], was treated with a slight excess of TDO to produce crude IC in essentially quantitative yield. Recrystallization from acetonitrile gave 1C monomer in 88 % yield, having mp. 133-134 °C. FT-IR (KBr, cm^{-1}) showed 1726 ($CH_3\mathit{CO}CH_2$), 1682 ($CH_2\mathit{CO}NH$), 1649 (C=N) and 1599 (phenyl). ^{1}H-NMR (ppm) showed δ 1.91 (p, J=5.5 Hz, 2H), 2.21 (s, 3H), 3.52 (m, 4H), 4.29 (t, J=5.0 Hz, 2H), 7.54 (d, J=9.0 Hz, 2H), 7.76 (d, J=8.75 Hz, 2H), and 9.43 (s, 1H). ^{13}C-NMR (ppm) showed chemical shifts at δ 21.81, 30.89, 42.42, 50.29, 65.12, 119.13, 127.68, 129.89, 139.61, 155.32, 164.00, and 204.28. Mass spectrometry showed m/z = 260.06 (calc.: 260.29)

Synthesis of N-Methyl-N-[4-(2-oxazolin-2-yl)phenyl]acetoacetamide 1D). Using a known procedure[26)] 4-Aminobenzonitrile was treated with a slight excess, on a molar equivalents basis, of methyl iodide in tetrahydrofuran solvent for 4 hr at room temperature. Removal of the THF and other volatiles, followed by recrystallization, gave a 76 % yield of 4-(N-methyl)aminobenzonitrile, mp. 85-87 °C. Using a published procedure [25)], the aforesaid substituted nitrile was treated with ethanolamine to obtain a 70% yield of 2-[4-(N-methyl)aminophenyl]oxazoline, mp. 145-147 °C. The compound is new to the literature. The aforesaid compound was treated with TDO to form the oxazoline (1D) having a methyl group attached to the nitrogen in the acetoacetanilide segment. The product was recrystallized from ethyl acetate, mp. 102-105 °C. FT-IR (KBr, cm^{-1}) showed 1740 ($CH_3\mathit{CO}CH_2$), 1716 ($CH_2\mathit{CO}NCH_3$), 1644 (C=N) and 1613 (phenyl). ^{1}H-NMR (ppm) showed δ 2.27 (s, 3H), 2.67 (s, 3H), 3.31 (s, 2H), 4.08 (t, J=9.2 Hz, 2H), 4.46 (t, J=9.6 Hz, 2H), 7.43 (d, J=8.8 Hz, 2H), and 7.99 (d, J=8.0 Hz, 2H). ^{13}C-NMR (ppm) showed chemical shifts at δ 21.11, 30.47, 42.55, 48.77, 64.25, 112.23, 122.15, 131.09, 147.23, 161.65, 169.48, and 205.68. Mass spectrometry showed m/z = 260 .05 (calc.:260.29)

Synthesis of the acetylacetoxy derivative of 2-(p-Hydroxyethoxyphenyloxazoline) (1E). The 2-(p-hydroxyethoxyphenyl)oxazoline used here was prepared by a previously described procedure15). A 250 ml, round bottom, three-neck flask, was charged with 2-(p-hydroxyethoxyphenyl)oxazoline, 8.28g (0.04 mol), 2,2,6-trimethyl-1,3-dioxin-4-one, 11.36g (0.08 mol), and 120 ml of xylene. The solution was stirred and heated at reflux, under nitrogen, for 5 hr. Evaporation of the solvent gave a high yield of the crude, solid product 1E. After washing with ethyl acetate, the β-ketoester substituted oxazoline product was recrystallized from petroleum ether to give a good yield of the desired compound (IE), mp. 72-75 °C. FT-IR (KBr, cm^{-1}) showed 1734 (wide peak for $CH_3\mathit{CO}CH_2$ and COO), 1649 (C=N) and 1610 (phenyl). ^{1}H-NMR (ppm) showed δ 2.05 (s, 3H), 3.33 (s, 3H), 3.94 (t, J=9.25 Hz, 2H), 4.10 (t, J=5.3 Hz, 2H), 4.25 (m, 4H), 6.77(d, J=5.25 Hz, 2H), and 7.09 (d, J=7.0 Hz, 2H). ^{13}C-NMR (ppm) showed chemical shifts at δ 30.11, 49.84, 54.81, 61.23, 65.90, 67.47, 114.18, 120.84, 129.89, 151.79, 160.67, 166.96, and 200.17. Mass spectrometry showed m/z = 291.11 (calc.:291.30).

Synthesis of Polymers

Synthesis of 1A polymer: A glass reactor was charged with 4.0 g of 1A monomer, 40 g of anisole solvent, and 0.15 g of methyl p-toluenesulfonate initiator, followed by purging with nitrogen and sealing under nitrogen. The polymerization was run 10 h at 135 °C. The polymer solution, on cooling, was combined with diethyl ether to precipite the polymer. The 1A polymer, collected by suction filteration, was washed with diethyl ether and dried under hard vacuum. The polymer had a glass transition termperature (T_g) of 35 °C, as shown by DSC.

Synthesis of the 1A-2-ethyloxazoline copolymer : Following the procedure used for polymerization of 1A, 4.0 g ea. of 1A and 2-ethyloxazoline (50/50, wt./wt.) were copolymerized in anisole, using 0.15 g of methyl p-toluenesulfonate initator. DSC showed the isolated and purified copolymer had a T_g of 11 °C.

Synthesis of the 1A-2-phenyloxazoline copolymer: Following the procedure used for copolymerization of 1A with 2-ethyloxazoline, 4.0 g ea. of 1A and 4.0 g of 2-phenyloxazoline (50/50, wt./wt.) were copolymerized in anisole, using 0.15 g of methyl p-toluenesulfonate initator. DSC showed the isolated and purified copolymer had a T_g of 21 °C.

Metal Complexing

The metal complexes of the monomer IA with inorganic salts, such as $CoCl_2$, $ZnCl_2$ or $CuCl_2$, were obtained as follows: Equal molar amounts of IA and the inorganic salts were combined in a flask charged with chloroform solvent. The mixture was refluxed for 45 minutes. After which time, the hot solution was quickly filtrated to rid the soluton of the non-soluble part. Evaporation of the solvent produced highly colored solid s for such things as the Co and and Cu complexes. The final product was extracted by acetone.

Results and Discussion

Table 1 provides a summary of the five monomers (1A-1E) prepared and characterized in this study. Scheme 1 shows the typical procedure used for preparing monomers IA, IB and IC. For monomer ID, it was necessary to first prepare the N-methyl derivative of p-aminobenzonitrile before treatment with diketene or TDO (Scheme 1) to obtain the desired monomer. The synthetic path for monomer IE is outlined in Scheme 2. All five monomers were prepared in good to excellent yields, with the results in Table 1 not optimized for any monomer. The structures of IA-IE were confirmed by FT-IR, NMR (^1H and ^{13}C) and mass spectroscopy.

Table 1. Monomers Prepared.

Monomers Structures	Yield %	MP. °C	Molecular Weight*	
			Calc.	Found
1A: R = 1,4-phenylene, X = NH, $R^1 = R^2 = H$, n = 0	88	171-172	246.26	246.10
1B: R = 1,3-phenylene, X = NH, $R^1 = R^2 = H$, n = 0	63	77-78	246.26	246.06
1C: R = 1,4-phenylene, X = NH, $R^1 = R^2 = H$, n = 1	88	133-134	260.29	260.06
1D: R = 1,4-phenylene, X = NCH_3, $R^1 = R^2 = H$, n = 0	64	102-105	260.29	260.05
1E: R = 1,4-phenylene, X = OCH_2CH_2O, $R^1 = R^2 = H$ n = O	67	72-75	291.30	291.11

* Mass spectra MW determined on a MAT-900 instrument

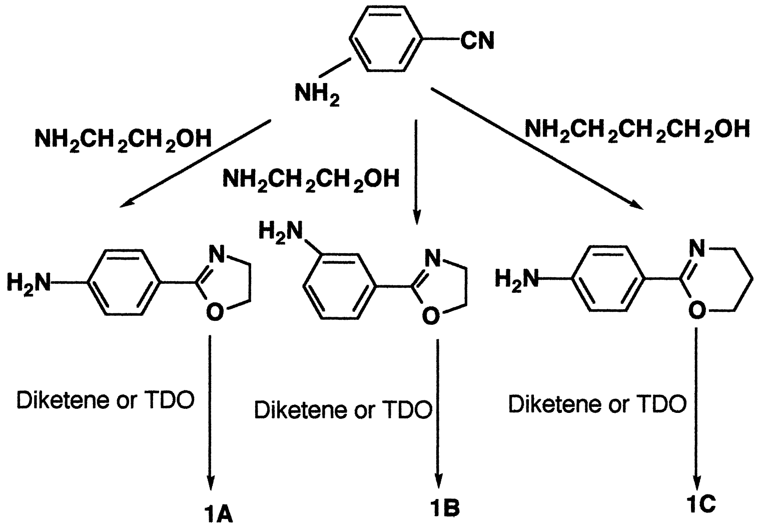
We find that multi-functional monomers of the type described may be homo- or copolymerized, using cationic initiators, to obtain cyclic imino ether (oxazoline) based copolymers having pendant acetylacetate, acetylacetamide or acetylacetanilide type residues. For example, it is possible to use a cationic initiator, such as methyl p-tolunesulfonate, to homopolymerize 1A or copolymerize 1A with 2-ethyl- or 2-phenyloxazoline, generating new metal complexing polymers or copolymers. While we do not show the reaction in this manuscript, the cyclic imino ether moieties may also be reacted with aryl OH or SH, CO_2H, etc., residues to give new monomers or polymers, via a step-growth reaction.

Monomers of the type disclosed (1A-1E), as well as the cyclic imino ether based polymers having acetylacetate, acetylacetamide or acetylacetanilide type moieties, readily form metal complexes. For example, the isolated 1A-$CoCl_2$ and 1A-$CuCl_2$ complexes have,bluish green and dark green colors, respectively. DSC showed that the described metal salts were stable, under nitrogen, up to ca. 270 °C.

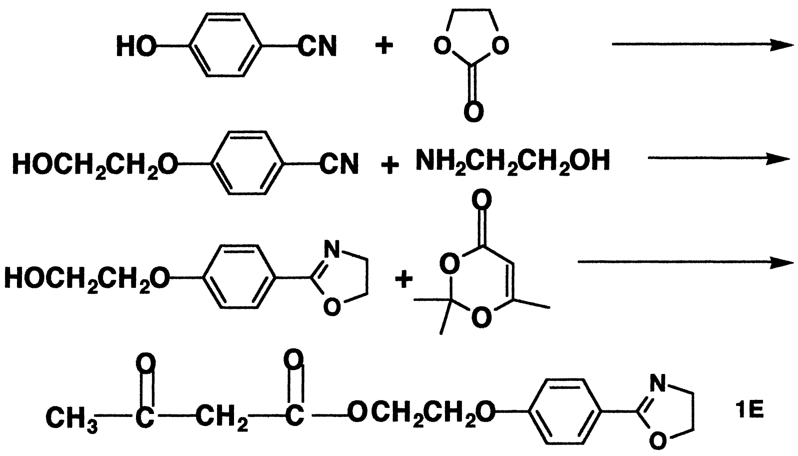
Aqueous solutions of the 1A or 1E copolymers, with 2-ethyl- or 2-phenyloxazolines, readily form metal chelates upon addition of inorganic salts. For example, the viscosities of the aqueous solutions of the 2-ethyloxazolie-1A and 2-ethyloxazoline-1E copolymers, in the presence of added $CoCl_2$, are higher than the corresponding copolymer solutions in the absence of added $CoCl_2$. As an illustration, an aqueous solution of the 2-ethyloxazoline-1A copolymer, having a 90:10 molar ratio, respectively, exhibited a 35% jump in viscosity compared to the same concentration of the copolymer having no $CoCl_2$, with both measurements made at the same spindle shear rate. The jump in viscosities is akin to what others have also observed for formation of other metal complexes in aqueous solutions16). Formation of a deep red colored solution, on addition of the $CoCl_2$ to the two aqueous solutions of the 1A and 1E copolymers, provided further evidence for complex formation.

Conclusion

We describe a procedure for preparing a large number of heretofore unreported cyclic imino ether monomers, functionalized with the β-ketoester group or the acetoacetamide or acetoacetanilide type residue. We show that these monomers may be homo- or copolymerized with other cyclic imino ethers, using cationic initiators, providing new polymers having metal complexing residues. Significant studies need to be done to determine the structures and utility of the wide variety of monomer and polymeric metal complexes which can be prepared with compounds such as 1A-1E. Further, studies need to be accomplished on using these monomers to crosslink and/or compatibilize various monomer / polymer combinations.



Scheme 1. Synthesis path for monomers 1A, 1B and 1C.



Scheme 2. Synthesis path for monomer 1E.

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