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Homo- and copolymers of methacryloylmalodiethylester, synthesis and behaviour

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Dedicated to Professor Paul Rempp on the occasion of his 65th birthday

Summary

Chelating polymers obtained by copolymerization of methacryloylmalodiethylester (MMDEt) with styrene, methylmethacrylate (MMA), N-vinylpyrrolidone (VPD) and N,N-dimethylacrylamide (DMAM) as well as the homopolymer of methacryloylmalodiethylester (MMDEt) have been investigated. Watersoluble chelating polymers derived from copolymerization with DMAM offer not only the possibility of a very fast removal of metal ions from aqueous solution, but are also insoluble after complexing certain metal ions and can therefore be separated by filtration. As additional investigations on the model acetyloylmalodiethylester (AMDEt) show, preferably hard metal ions such as Mg^{2+}, Ca^{2+}, Al^{3+} and Cu^{2+} with an ionic radius up to 1 Å are chelated by the enolic form of the ß-ketodiester. The number of ligands for a metal ion corresponds to its valence.

Introduction

1,3-Dicarbonyl compounds are known to form very stable and slightly polar enolate salts with polyvalent metal cations, better known as metal chelates for which those of acetylaceton are prominent examples. Anions of 1,3-dicarbonyl esters like acetoacetate or diethyl malonate easily react with acyl halides to give acylation products. Starting from diethyl malonate a chelate forming monomer is available by reaction with acryloyl and methacryloyl chloride, respectively, as has been shown by EGLE /1/. He also reported on some chelate forming properties of resulting polymers, but on the whole a more detailed investigation on monomer and polymerization behaviour as well as metal ion chelates of these compounds was desirable.

Experimental

Styrene (BASF) and methylmethacrylate (Degussa) were purified by destillation under reduced pressure. AiBN (Aldrich) was recrystallized from diethyl ether. N-vinylpyrrolidone (Fluka), N,N-dimethylacrylamide (Fluka), diethyl malonate (Aldrich) and

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acetyl chloride (Fluka) were used as supplied.

Methacryloyl chloride was synthesized in the common way /2/ by reaction of methacrylic acid with thionyl chloride under DMF catalysis.

Methacryloylmalodiethylester was synthesized as described by EGLE /1/; in the case of acetyloylmalodiethylester acetyl chloride instead of methacryloyl chloride was used.

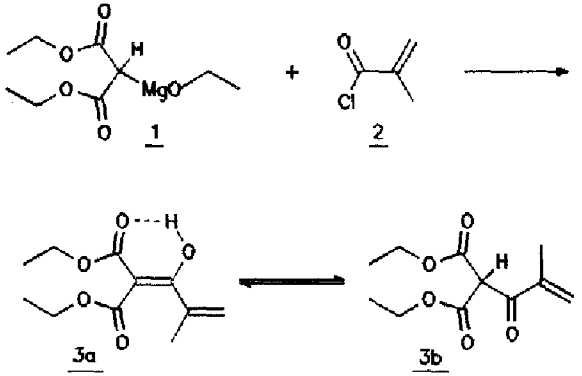
The silylation of the methacryloylmalodiethylester was carried out under nitrogen with diethyl ether as solvent and a slight excess of hexamethyldisilazan (HMDS) as silylation agent. After stirring over 3 d at room temperature the solution was separated from the residue by filtration and the ether was evaporated. The crude liquid product was purified by destillation under reduced pressure (51°C at 2 mbar) giving a colourless liquid, which crystallizes spontaneously as colourless needles with a melting point of 64,5°C.

All polymers were synthesized by free radical polymerization with AiBN as initiator at 60°C with dry 1,4-dioxane as solvent in sealed glass tubes under an argon atmosphere.

Results and Discussion

Investigations on poly(methacryloylmalodiethylester)

Methacryloylmalodiethylester (MMDEt) 3 was synthesized by acylation of the ethoxymagnesium compound of diethylmalonate 1 with methacryloyl chloride 2 /1/. Due to keto-enol tautomerism, MMDEt gives 5% of the enolic 3a and 95% of the keto form 3b /3/.



As shown by GPC investigations, free radical polymerization of MMDEt in 1,4-dioxane gives low molecular weight (8000 g/mol) polymers insoluble in water. The low molecular weight is a result of chain transfer reactions of the proton in the enolic form of the molecule during polymerization. To increase molecular weight and avoid losses in yield by small oligomers, the trimethylsilyl group was used as protecting group for the enolic OH-group. In fact the blocking of the OH-group gives higher yields and molecular weights, but the removal by hydrolysis of the trimethylsilylenolether causes decarboxylation of the β-ketodiester and therefore the loss of chelating properties in the polymer. The low molecular weight polymer decarboxylated after treatment with acids in the typical way of β-ketoesters. Decarboxylation occured also at temperatures above 100°C as shown by thermogravimetric measurements.

Chelating behaviour of poly(methacryloylmalodiethylester)

It is generally accepted that the metal ion is chelated by the enolic form of the β-ketoester /4/. The β-ketodiester preferably replaces all anions of the metal salt but also a partial exchange of ligands is possible. This partial exchange is caused either by an excess of metal ions or by sterical restriction, which may occur in polymers. Due to the alteration of the environment by chelating a metal ion a shift of the carbonyl bands in the UV/Vis- and IR-spectra is expected. Indeed the UV/Vis-spectrum of poly(MMDEt) in THF shows a red shift of the carbonyl functions from 253 nm to 273 nm by chelating Cu^{2+}. The band of the chelate was determined by derivative spectroscopy as not all chelating groups were involved due to sterical restrictions. IR-spectroscopic measurements on the Cu^{2+}-polymer chelate also show a significant alteration in the carbonyl bands.

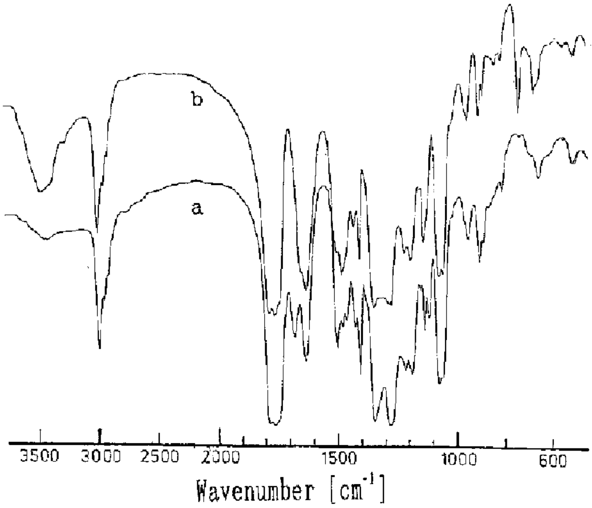


Fig. 1: Infrared absorption of poly(MMDEt) (a) and poly(MMDEt) chelated with Cu^{2+} (b).

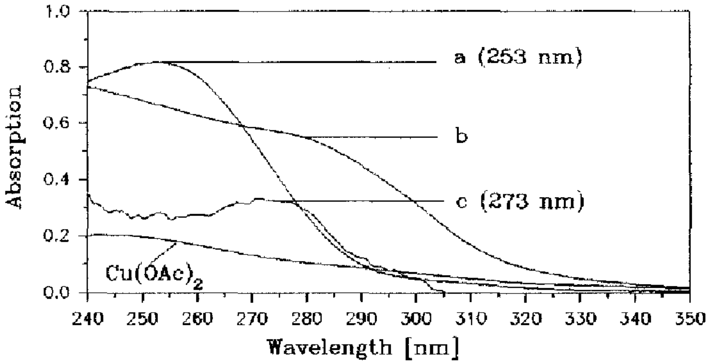


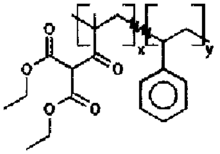
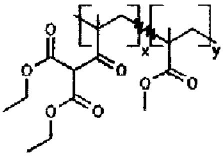
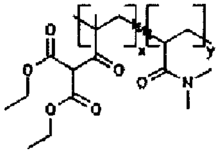
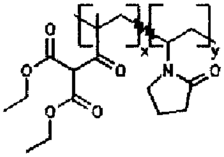
Fig. 2: UV/Vis-spectra of poly(MMDEt) (a), poly(MMDEt) chelated with Cu^{2+} (b) and its derivative spectrum (c).

To avoid sterical effects AMDEt was used as model compound for further investigations on chelating abilities towards different metal ions. The spectroscopical data obtained with AMDEt and its chelates in methanolic solution are in accordance with those of poly(MMDEt). Investigations on different metal ions show that not only chelates but also complexes are formed, depending on size and polarizability of the metal ion. Hard, Lewis acid like metal ions as Mg^{2+}, Ca^{2+}, Al^{3+} and Cu^{2+} with an ionic radius up to 1 Å are chelated by the enolic form of the β-ketodiester. As the formation of the enolic form is an equilibrium, the β-ketodiester is almost quantitatively transformed into the enolic form and the UV/Vis-spectra show a shift in the carbonyl band from 251 nm to 264 nm (Cu^{2+}: 273 nm). The chelates are stable against hydrolysis. The chelates only can be destroyed by addition of acids, which causes the decarboxylation of the β-ketodiester. Several more soft metal ions like Co^{2+}, V^{3+} and Fe^{3+} show no shift but an additional band at 280-290 nm in the UV/Vis-spectra and are striking their intensitive colours. They are less stable against hydrolysis and are much better soluble in solvents with hydroxylic groups than the chelates of the hard metal ions. The alkali metal ions show no effect in the UV/Vis-spectra but there seems to be an exchange reaction with the proton of the enolic form of the β-ketodiester.

Influence of copolymerization on solubility

An important condition for fast chelating kinetics is a well defined solubility of the polymer in the choosen solvent. To reach a fairly well solubility in nearly all common solvents, many former authors used different chelating monomers to form polymers with the desired properties. In our work always the same chelating monomer was used, and the hydrophobic or hydrophilic character of the polymer was varied by the amount of an additional monomer by copolymerization. The investigated comonomers were styrene for unpolar organic solvents, methylmethacrylate (MMA) for polar organic solvents and N,N-dimethylacrylamide (DMAM) as well as N-vinylpyrrolidone (VPD) for very polar organic solvents and water. VPD turned out to be unsuitable to increase the solubility in water because of disadvantageous r-parameters. The r-parameters were obtained by the method of FINEMAN-ROSS /5/ and are listed in table 1.

Tab. 1: Reactivity ratios of MMDEt towards different monomers at free radical polymerization in 1,4-dioxane at 60°C with AiBN as initiator.

monomer pairs	r-parameters	structural units
MMDEt Styrene	$r_1 = 0{,}22 \pm 0{,}002$ $r_2 = 0{,}23 \pm 0{,}005$	
MMDEt MMA	$r_1 = 0{,}60 \pm 0{,}006$ $r_2 = 0{,}79 \pm 0{,}01$	
MMDEt DMAM	$r_1 = 0{,}68 \pm 0{,}07$ $r_2 = 0{,}59 \pm 0{,}09$	
MMDEt VPD	$r_1 = 1{,}98 \pm 0{,}04$ $r_2 = 0{,}001 \pm 0{,}02$	

Investigations on watersolubility

Watersoluble chelating polymers are of great interest for the very fast removal of metal ions in wasted water, therefore the solubility of several polymers derived by copolymerization with DMAM will be discussed here. As MMDEt forms water insoluble and DMAM watersoluble polymers, the watersolubility of the copolymer should increase with the amount of DMAM. Polymers with hydrophilic and hydrophopic groups may exhibit a lower critical solution temperature (LCST) above which the polymer separates from an aqueous solution for which poly(N-isopropylacrylamide) is a well studied example /6/. The reason for this effect is the loss of hydrogen bonds with increasing temperature, which affects the sensitive balance between hydrophilic and hydrophobic parts in the polymer. In the case of chelating polymers it may be possible to lower this temperature by addition of ions, because chelating a metall ion, MMDEt not only looses hydrogen bonds, but also crosslinking appears due to the fact that a polyvalent metal ion is chelated by more than one ligand. Indeed, investigations on solubility under this aspect confirm that the copolymer not only looses its solubility but also forms extended networks which can easily be separated from the aqueous solution by filtration. The critical temperature was determined by turbidity measurements. For a copolymer containing different amounts of DMAM the 50% transmission data (solution 100%, total insolubility 0%) of the polymer and the Cu^{2+} chelate are compiled in table 2.

Tab. 2: Temperature of separation of poly(DMAM-co-MMDEt) and its Cu^{2+}-chelate in water; depending on the amount of DMAM.

	90% DMAM	84% DMAM	78% DMAM	74% DMAM	60% DMAM
polymer	83°C	50°C	soluble	soluble	insolub.
chelate	57°C	23°C	≈4°C	insolub.	insolub.

As the table shows, copolymers with about 75% DMAM can be used for the removal of metal ions from aqeous solution. The solubility increases by the amount of DMAM as expected. A possible explanation of the fact that the polymers with 74% and 78% DMAM show no LCST could be the formation of micellar structures.

Conclusions

Methacryloylmalodiethylester as a polymer supported ligand not only offers the ability of chelating certain metal ions but also a variety in solubility. The solubility can be varied from unpolar organic solvents up to polar solvents like water by simple copolymerization with different monomers. The fact that the removal of the chelated metal ions by acids causes decarboxylation of the ligand, disables these polymers for regeneration. But the capability of such copolymers to chelate different hard metal ions which are of great interest in ceramic and semiconducting applications, leads to a broad variety of organometallic networks with interesting chemical and physical properties. Under this aspect further investigations are in progress.

Acknowledgements

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