Imidazolium Hardeners

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Abstract

A new class of peptide coupler type crosslinking agents are described. The representatives of the new hardener class are fast hardeners without he adverse effect of low stability. A hardening pathway is also proposed. The hardening pace and the dependence of hardening with pH is described.

Introduction

Gelatin is a common component of each silver halide based photosensitive material as the major part of the binder system. Gelatin is an excellent protective colloid for the silver halide grains, but for conferring good mechanical properties and processeability it needs to be crosslinked. By crosslinking the gelatin, a tridimensional matrix is formed which has a higher melting point than the initial gelatin. During crosslinking of the gelatin new chemical bonds are formed between a crosslinking agent (hardener) and the gelatin. From crosslinking standpoint gelatin contains amine and carboxyl groups, which both can serve as crosslinking sites.

$$2\ \text{Gel-NH}_2 + \text{X} \longrightarrow \text{Gel-NH-X-NH-Gel} \qquad (1)$$

$$\text{Gel-NH}_2 + \text{Gel-COOH} \longrightarrow \text{Gel-CO-NH-Gel} + \text{Y}' \qquad (2)$$

In case (1) because only amine groups are involved in hardening "X" is called an amine hardener. Depending on the nature of the "X" group, the hardening speed and the strength of the hardened layer will be different. In the second case, because a new peptide bond is formed "Y" is called a peptide type crosslinking agent. It is necessary to note the basic difference between the two types of hardeners. Amine cross linkers will be incorporated in the final binder matrix and they always bond two amine groups. Peptide type couplers will form a new amide bond and they will not be incorporated in the binder matrix. In case of peptide couplers it is true that the hardener will not be incorporated into the binder matrix, but it's decomposition product after crosslinking (Y') will remain in the film structure and it may influence the sensitometric properties of the film, if it is not inert. The different compounds developed for gelatin hardening are described in literature.[1] Hardeners containing the imidazolium ring were described only recently.[2,3,4] Because of their remarkable hardening effect this new hardener class will be studied farther.

Experimental

Materials

The starting imidazol derivatives, various carbonyl chlorides, acid chlorides and triethylamine were from Aldrich and were used without purification. Acetone was certified reagent grade from Fisher.

General Techniques.

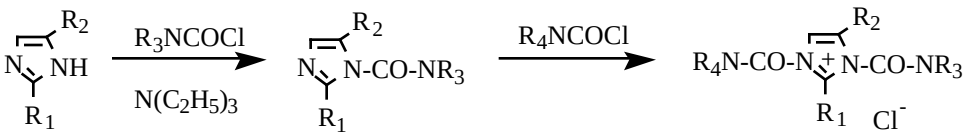
Melting points were taken on a capillary melting point apparatus and are uncorrected. Proton and C^{13} NMR spectra were determined on a Hewlett Packard Gemini 300 Spectrometer. The data are available upon request.

Hardener Synthesis.

The reaction scheme is shown in Scheme 1. 0.1 M of the corresponding imidazole derivative was dissolved in 100 ml acetone.

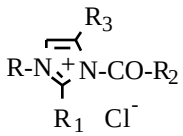
After dissolution 0.1 M of triethylamine was added and the solution was brought to reflux. At reflux 0.1 M of the corresponding carbonyl chloride was added in 30 min. A white precipitate of triethylamine hydrochloride was formed after the addition. The reaction mixture was refluxed for 3 hours, cooled down to room temperature and filtered next day. The precipitate was rinsed 3 times with acetone. The first filtrate and the washings were unified and brought to reflux. At reflux 0.1 M of the corresponding carbonyl chloride was added at once. After the addition the mixture was refluxed for 3 hours, cooled to room temperature and filtered next day. The precipitate was rinsed with acetone and dried in vacuum dessicator. In case of N-substituted imidazole derivatives only the 2nd step of Scheme 1. was done to get the corresponding hardener.

Scheme 1.



The representative new hardeners, synthesized according to the above procedure are given in Tab 1.

Table 1. New Peptide Couplers



#	R	R1	R2	R3
I	H3C-	H-	-N(CH3)2	-H
II	C6H5CH2-	H-	-N(CH3)2	-H
III	H22C10-	H-	-N(CH3)2	-H
IV	H2C=CH-	H-	-N(CH3)2	-H
V	H2C=CH-CH2-	H-	-N(CH3)2	-H
VI	(CH3)2NCO-	H-	-N(CH3)2	-H
VII	(CH3)2NCO-	H3C-	-N(CH3)2	-H
VIII	(CH3)2NCO-	H-	-N(CH3)2	-H3C-
IX	(CH3)2NCO-	H3C-	-Morpholino	H-
X	H25C12CO-	H-	-N(CH3)2	H-
XI	Morpholino-	H3C-	-Morpholino	H-

Gelatin Hardening

For evaluation of the new hardeners an 8% gelatin solution with pH adjusted to pH = 5.8+/-0.05 was treated with different amounts of hardeners. The samples were Myer rod coated on polyester base, dried at room temperature and evaluated 24 hr after coating. The degree of hardening, expressed as melting time for the representative new hardeners are given in Fig.1. Compounds (VII) and (VIII) are superimposed.

In conclusion the new compounds (IV), (VI), (VII), (VIII) and (XI) are very effective crosslinking agents. Compounds (I) and (V) are less active and (III) has even lower activity. In case of (III) because of the attached long alkyl rest, the hardener has the properties of a surfactant.

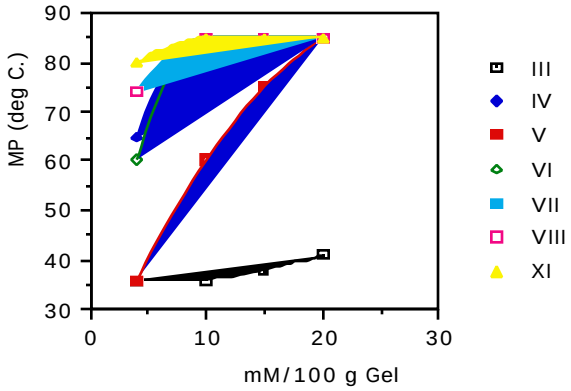


Fig.1.

Stability of the New Hardeners

Because of their high reactivity, the fast hardening agents generally have low stability in aqueous solution. In some cases in a 24 hour period 50% of the initial hardener could be decomposed. From a manufacturing standpoint a hardener with higher solution stability will definitely be advantageous. The stability of a 10% aqueous solution at room temperature for some of the new hardeners is given in Fig. 2.

It is obvious that the new peptide coupler type hardeners are superior as aqueous solution stability to the ones described in literature.

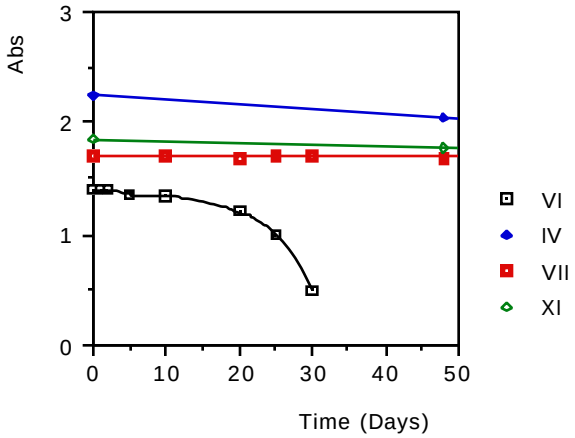


Fig. 2.

Hardening pH

The imidazolium type hardeners are quaternary salts it is expected that they will be decomposed at high pH. For a good hardening efficiency the optimum pH range need to be determined. The influence of solution pH on degree of hardening for the amount of 5 mM hardener/100 g gel. is given in Fig. 3.

The degree of hardening, expressed as MP, in case of (XI) is practically not effected by pH in the domain studied, while in case of (VI) is very pH dependent. As high pH stability, there's a basic difference between the above hardeners; while (VII) and (XI) are 2-methyl imidazolium derivatives, in case of (IV) and (VI) the position two of the imidazolium ring is unsubstituted. According to[5] these derivatives will de irreversibly decomposed at high pH by ring opening. A ring opening during hardening/grafting with the above compounds was observed also.[6] In case of 2-alkyl-imidazolium derivatives such a decomposition will not occur.

In order to get a better understanding of hardening phenomena at different pH values, 8% gelatin solutions with different pH values were treated with 10 mM (XI)/100 g gel. The solutions were kept at 40 deg C. and the viscosity increase was monitored. The results are given in Fig. 4.

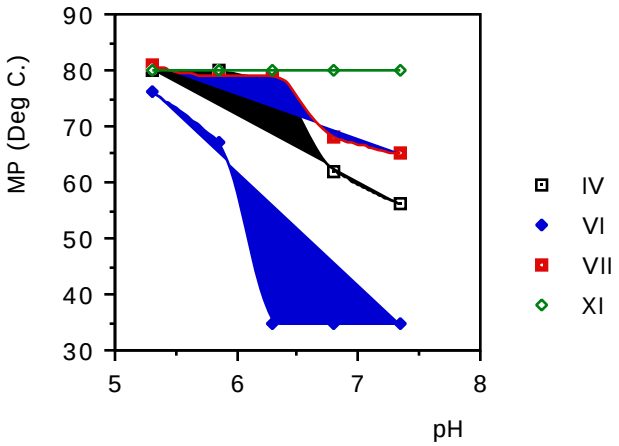


Fig. 3.

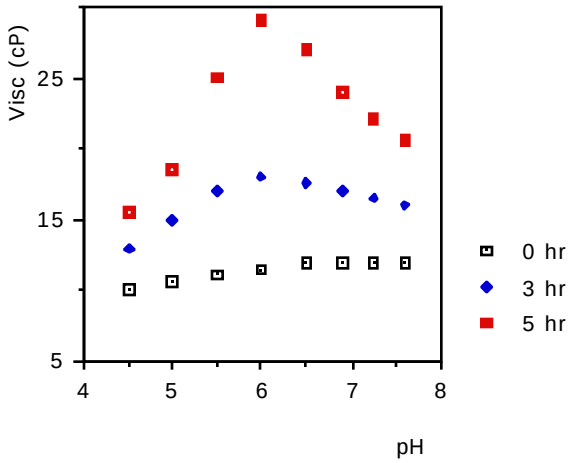


Fig. 4.

The viscosity increase in time, at constant gelatin and hardener concentration is the highest at pH=6. In order to correlate the gelatin crosslinking in a coated sample and the viscosity increase, a similar experiment was run with the hardener concentration of 5 mM (XI)/100 g gel. Samples were taken time to time from the mixture and coated. The hardening degree, expressed as MP in function of solution pH and time is given in Fig. 5.

It is interesting to note, that by low pH treatment of the coated and dried sample, the optimum pH interval for hardening widens as it is expressed in Fig. 6.

Hardening Reaction Pathway

For similar peptide coupler type hardeners two mechanisms were suggested. According to one mechanism[7] the peptide bond is formed through an anhydride type intermediate resulted by reaction of carboxyl group and the peptide coupler. This mechanism explains the formation of the final peptide bond, but it is very unlikely that in diluted aqueous solution the anhydride intermediate could be formed.

According to another mechanism[8] the hydroxyl group of the gelatin chain will react in the first step with hardener to form a dimethylcarbamyl ester.

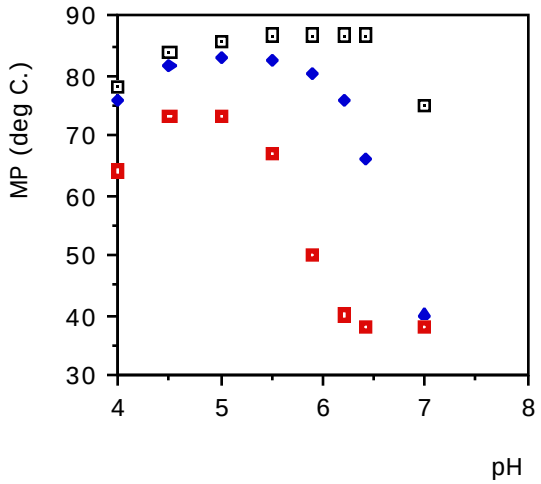


Fig. 5.

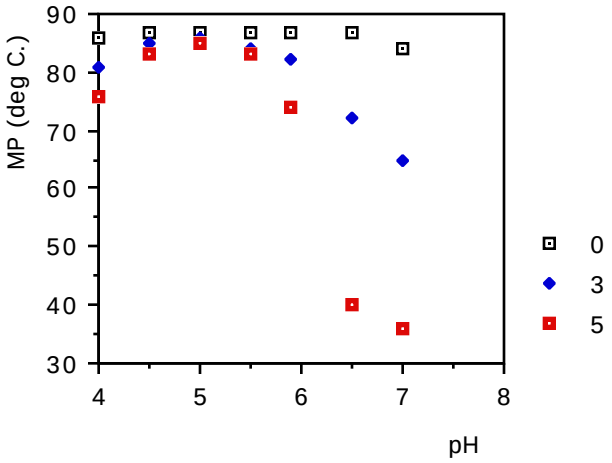
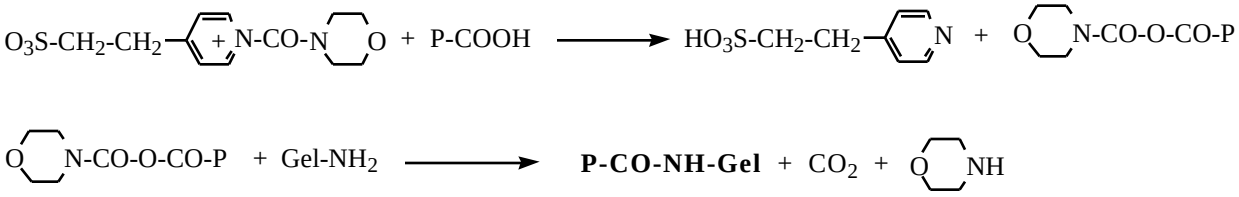
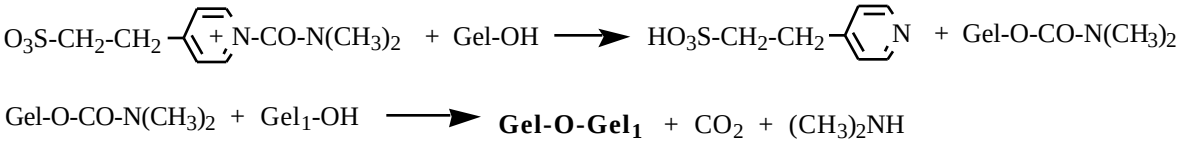


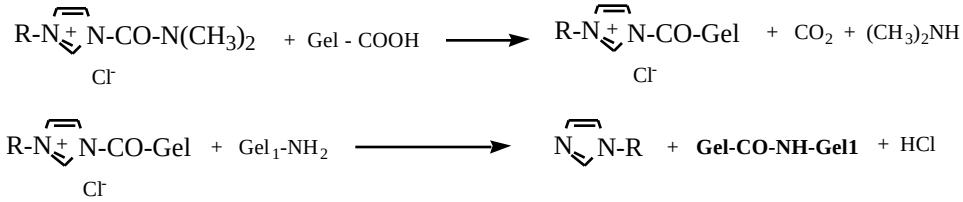
Fig. 6.



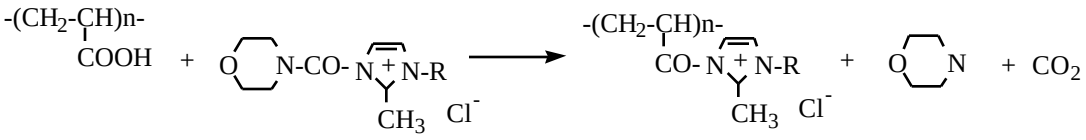
The intermediate ester will react with another hydroxyl group to form an ether bond and to liberate dimethylcarbamic acid. It is to be noticed that according to this reaction pathway no peptide bond is formed.



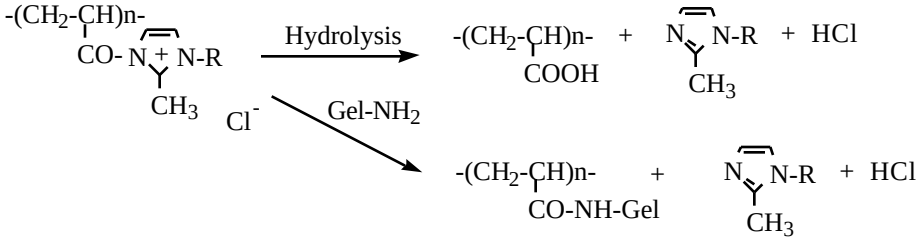
Another, more likely reaction pathway is the following:



In the first step of the reaction one carboxyl group of the gelatin will react with the hardener with the formation of an amide type activated intermediate. In the second step this intermediate will react with an amine group of the gelatin chain. A new amide bond will be formed which will crosslink the gelatin. The activated intermediate may not react only with amino groups of the gelatin, but with other nucleophiles also. This is very important, because it leeds to possibilities to graft additional useful groups to the gelatin backbone. In certain cases the activated intermediate is not able to react with an amine group of a gelatin molecule to form a new peptide bond. It is necessary to mention, that the imidazolium type hardeners may react in the first step with a carboxyl group different from the gelatin. This assumption was taken in account to prove the proposed hardening pathway.



XI-A



XI-B

Corresponding amounts of (XI) and poly(acrylic) acid were mixed in D2O and the C^{13} NMR spectra was recorded immediately after mixing. Then the mixture was heated to 60 deg C and maintained at the same temperature for 20. Cooled down and the NMR spectra recorded again. In the initial spectra positions 4 an 5 of (XI) being equivalent there's only one signal (123.102 ppm). After the reaction of (XI) with poly(acrylic) acid the reaction mixture consists of unreacted (XI), (XI-A) which is unsimmetric and (XI-B) unsimmetric also. In the second spectra recorded after the reaction was compleated all the three signals, corresponding to the above species, were recorded. (122.00 and 122.577 ppm) Any attemptions to make the anhydride type intermediate mentioned in from morpholinocarbamyl chloride and poly(acrylic) acid in similar conditions failed.

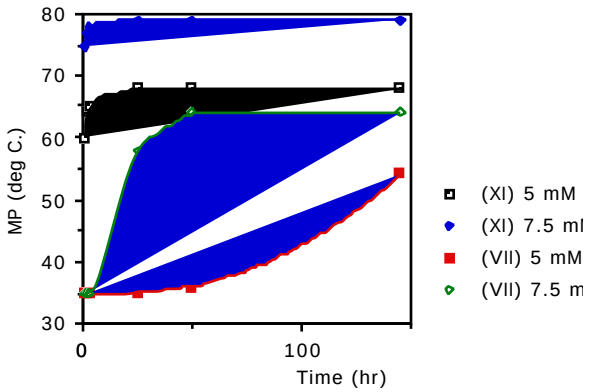


Fig. 6.

Hardening Pace

Both for developing new products and controlling the manufactured ones hardening speed in important. Sensitometric properties of the photosensitive materials are strongly influenced by hardening.

The imidazolium type hardeners are fast acting ones, but the actual hardening pace depends on the individual structure of the hardeners. The evolution of hardening in time for (VII) and (XI) is given in Fig. 5. The amount of hardener used refers to 100 g of gelatin. It is easy to see that in case of (XI) the hardening is completed in less than 24 hr after coating. This is an excellent result, considering the also stability of the aqueous solution of (XI)

Conclusions

New peptide coupler hardeners were described with excellent hardening properties.

A new hardening pathway is also proposed.

References

* Present Address:DuPont Nylon Intermediares R&D, SRL, P.O. Box 1089, Orange TX 77630

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