Chemical Modification of Gelatin Emulsion Light-Sensitive Layers by Glycidilamines

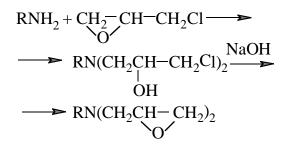
P. M. Zavlin, L. L. Kuznetsov, I. G. Chezlov, N. K. Ryasinskaya St. Petersburg Institute of Cinema & TV, St. Petersburg, Russia

Abstract

The work done was devoted to the problem of the purposeful modification of gelatin emulsion light-sensitive layers with glycidylamines, including the development of new chemical gelatin modifiers, the determination of the relationship between their structure and modified gelatin properties as well as the complex investigation of the conditions of their usage as a part of real black-and-white and color emulsion layers.

Producing Oxirane Gelatin Modifiers on the Basis of Mono- and Diamines of Aliphatic and Aromatic Series

The most efficient way of producing glycidylamines is the chlorohydrin method based on the reaction of epichlorohydrin with amines. In order to obtain reliable data on the relationship between the glycidylamine structure and reactivity, a great number of these substances were synthesized. The synthesis was carried out to the following scheme:



Alkyldiglycidylamines were produced at 30-32°C. A distinguishing feature of the synthesis was that no special solvents were used, it was the excess of epichlorohydrin that served as an effective solvent. This allowed to obtain a greater yield of final products with a lower content of impurities. Diglycidylamines of the aliphatic series are transparent liquids which polymerize when kept in air. It results in the necessity of their stabilizing with aprotic solvents. The synthesis of aromatic diglycidylamines was affected in an anhydrous medium at 80-90°C with the excess of epichlorohydrin.

As a result of this work a number of polyglycidylamines of aliphatic and aromatic series have been synthesized. Diglycidyl derivatives of ethylendiamine and tetraglycidylpolymethilendiamines were obtained from epichlorhydrin and diamines according to the following reaction:

$$\begin{array}{c} HN-M-NH + CH_2-CH-CH_2CI \longrightarrow \\ R & R \\ CICH_2-CH-CH_2N-M-NCH_2CH-CH_2CI \\ OH & R & R \\ CH_2-CH-CH_2N-M-NCH_2CH-CH_2 \\ O & R & R \\ O & R & R \\ O & O \\ \end{array}$$

One of the main factors responsible for the reactivity of glycidylamines is their basicity, so it was important to evaluate the basicity of the synthesized compounds of glycidylamine series.

The influence of glycidylamine structure on its basicity was studied for a variety of glycidyl derivatives of monoamines having different number of epoxygroups. The basicity of aliphatic glycidylamines readily soluble in water was measured by means of potentiometric titration. Glycidylamines of the aromatic series having low water solubility were studied using the spectrophotometric method. The experimental data given in Table 1 show that N-glycidylamines basicity with regard to nitrogen atom is considerably higher than that with regard to oxygen but it is lower than the basicity of corresponding amines.

| Glycidylamine | pK_{NH^+} | $\sigma^{*}_{gl.}$ | No |
|--|-------------|--------------------|----|
| CH ₃ N(Gl) ₂ | 6.50 | 0.472 | 1 |
| $C_2H_5N(Gl)_2$ | 6.85 | 0.468 | 2 |
| $i-C_3H_7N(Gl)_2$ | 7.13 | 0.470 | 3 |
| $n-C_4H_9N(Gl)_2$ | 6.93 | 0.471 | 4 |
| CH ₂ =CHCH ₂ N(Gl) ₂ | 6.13 | 0.460 | 5 |
| $HOCH_2CH_2N(Gl)_2$ | 5.82 | 0.478 | 6 |
| HOCH ₂ CH ₂ CH ₂ N(Gl) ₂ | 6.28 | 0.471 | 7 |
| $N(Gl)_3$ | 4.98 | 0.472 | 8 |
| $C_6H_5CH_2N(Gl)_2$ | 5.77 | 0.476 | 9 |
| $C_6H_5N(Gl)_2$ | 2.94 | 0.456 | 10 |
| $p-CH_3C_6H_5N(Gl)_2$ | 3.02 | 0.437 | 11 |

Table 1. Basicity of glycidylamines

The basicity of glycidylamines of aliphatic series is within a range 5-7 in pK_{NH+} values, while that of glycidylarylamines is considerably lower due to the electronoacceptor influence of the aromatic center. Therefore in media close to neutral aromatic glycidylamines are in unprotonated form and aliphatic glycidylamines are, to a great extent, protonated. The comparison of the basicity values for glycidylamines and parent amines shows that glycidyl group is a rather strong electron acceptor. There is a correlation between the basicity of tertiary amines and electron withdrawing properties of substitutes linked to a nitrogen atom, which can be expressed by Hall and Folkers equation.

The data on the basicity of glycidylamines allowed to determine the values of the inductive constant for the glycidyl substitute (σ_{G1}) using σ^* values for alkyl and aryl groups. The average value of σ_{G1} obtained for the range of pK_{NH+} compounds (1-9, 12) is 0.471 and for all range of glycidylamines concerned it is equal 0.467. The knowledge of the inductive constant value for glycidyl group makes it possible, using the relation between pK_{NH+} and $\Sigma\sigma^*$, to calculate the basicity value for N-glycidylamines of practically any structure.

Unlike glycidyl derivatives of monoamines, polyglycidyl derivatives of diamines have two protonation centers with regard to nitrogen atoms and two constants of basicity correspondingly.

Measuring the basicity of polyglycidiamines was carried out in the way similar to that for monoamines. The results are presented in Table 2. The data obtained make it possible to conclude that the basicity of tetraglycidylamines is 5-10 thousand times lower than that of corresponding diamines. These data are necessary for the interpretation of the results of the kinetic studies as well as for the explanation of the reactivity of di- and polyglycidylamines.

Table 2. Basicity of tetraglycidyldiamines Gl₂N-M-NGl₂, 20°C.

| М | Tetraglycidyldiamine | | |
|-----------------|----------------------|-------------------|--|
| IVI | $pK_{\rm NH+}$ | pK _{NH+} | |
| | (I) | (II) | |
| $(CH_2)_3$ | 7.05 | 4.55 | |
| $(CH_2)_4$ | 7.40 | 5.38 | |
| $(CH_2)_6$ | 7.72 | 5.90 | |
| $\neg \bigcirc$ | 2.40 | 0.54 | |

The effective using of oxyrane compounds as hardeners is only possible taking account of their reactivity as regards gelatin and other components of light-sensitive layers. So far, however, the research into the development of new light-sensitive materials has often been done without considering the kinetic characteristics of gelatin at the stage of hardening. In the connection the study was made on the reaction between oxirane compounds and gelatin in aqueous solution.

Since gelatin emulsion layers are characterized by a rather high moister content, the structuring process is always accompanied by the hydrolysis of epoxy hardener contained in them, a corresponding glycol being formed. Thus, in the oxirane-water-gelatin system two parallel reactions take place which in case of diglycidylamines can be expressed by the following scheme:

$$N(CH_{2}CH-CH_{2})_{2} \rightarrow \begin{pmatrix} k_{hydr} \\ H_{2}O \\ & H_{2$$

Hence, the effective rate constant measured in terms of oxirane consumption is:

$$K_{eff} = k_{hydr} + k_{NuH} \bullet [GNH_2]$$

where k_{NuH} - the experimental second order rate constant for the reaction of oxirane with gelatin (GNH₂), k_{hydr} - the experimental first order rate constant for the reaction of oxirane with water.

Than, having measured the effective rate constant and that for hydrolysis, it is possible to determine the rate of the reaction between oxirane and base (gelatin) despite the parallel hydrolysis taking place.

The kinetic studies of the interaction between glycidylamines and water show that, regardless of the number of epoxy groups in a molecule, the time variation of epoxide concentration follows strictly the first order equation up to the full completion of the reaction. This suggests that the splitting of the first and successive epoxy groups proceeds at the same speed.

The kinetic regularities of the interaction of these compounds with nucleophilic reagents over a wide pH range are determined, first of all, by the presence in their structure of two protonation centers. In order to determine the mechanism of this interaction, the kinetic studies were made beginning with the reaction of glycidol and its ethers containing only one center of protonation – oxygen atom of oxirane cycle.

The hydrolysis of glycidol, vinylglycidyl ether of ethylene glycol (vinylox) and diglycidyl ether was studied at 70°C over the pH range 2.20-11.61. The reaction rate remains practically constant within pH range ~5-10. At pH>10 and <5 the hydrolysis rate increases. This relationship is usual for oxiranes whose interaction with water goes through both the neutral and O-protonated forms. As this takes place, the water molecule or hydroxide-anion can act as a nucleophilic agent splitting the epoxide oxirane cycle.

The hydrolysis rate of the compounds involved is the same over the pH range studied. Hence, the substitution of hydrogen atom in glycidol hydroxy group does not influence the distribution of electron density in the oxirane cycle and the reactivity of the latter. Measuring the hydrolysis rate of diglycidyl ether at different temperatures allowed calculating the observed activation energy of the process. For the pH range where the rate practically does not depend on pH the value of E_a was equal to 84.7 kJ/mol.

Unlike the dependence of the hydrolysis of glycidol and its derivatives on pH, triglycidylamine and aliphatic glycidylamines hydrolyze with maximum rate at pH 6-8. The pH increase up to \sim 10 and its reduction to \sim 3 results in the reduction of the reaction rate. The dependencies observed are easily explained by the mechanism according to which the reactive forms of glycidylamine are neutral, Oprotonated and O,N-diprotonated ones. At pH>~10 the total reaction rate is determined by the rate of oxirane scission under the action of hydroxide-anions. Within the range ~10-~3, O-protonated form is reactive. At pH lower ~3 reactive form of oxirane is O,N-diprotonated one.

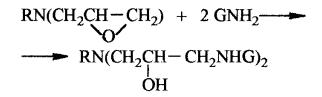
The results of kinetic studies make it possible not only predict the resistance of glycidylamines to hydrolysis but to calculate the rates of their reactions with nucleophilic reagents in aqueous solutions. In order to study the process of the reaction between oxirane compounds and gelatin which is known to proceed with amino and guanidine groups of this polymer, the kinetic investigations of the reactions in aqueous amine solution model system were carried out. Taken as model compounds were aliphatic amines having the basicity close to that of gelatin amino groups. With the excess of nucleophilic reagent its concentration remains practically constant in the course of the reaction and the product $k_{\text{NuH}} \cdot [\text{NuH}]$ is the first order rate constant which depends on the reactivity and concentration of the unprotonated amine form. The results of the kinetic studies of the reaction between glycidol and aqueous solution of morpholine reveal the increase of the reaction rate with the increase of pH. It is in the full agreement with the decrease in the degree of the amine protonation. This conclusion is confirmed by the data on the kinetic study of the reaction between triglycidylamine and aqueous solution of diethylamine. In the reaction of gelatin its basic groups are protanated depending on pH in the same way as amines. For this reason the rate of the reaction of oxirane compounds with gelatin increases with pH.

It has been observed that in neutral and slightly alkaline media diglycidylaniline reacts with gelatin much slower than diglycidylethanolamine, triglycidylamine and tetraglycidylhexamethylenediamine do. As pH increases the difference in reactivities decreases and at pH>~10 all four compounds react with gelatin at about the same rates. These dependencies, which are due to the differences in glycidylamine basicities with regard to oxygen atom, coincide completely with those observed during the hydrolysis.

Thus, it has been found that a di- (poly-) oxirane compound, when added to the gelatin solution as a hardener, is consumed for hydrolysis, which results in the lowering of its effective concentration. So it seemed important to determine the part of epoxide consumed effectively for gelatin hardening. The examination of the data obtained shows that this part increases with the increase in pH. While at high pH values (~9-10) the effectiveness of hardener using is rather high (70-80%). In the media close to neutral it decreases considerably (to ~10-20%). These conclusions have been made as applied to the condition studied (aqueous gelatin, 70°C). Under real conditions (room temperature, gelatin gel) the rate constants of epoxide reaction with both water and gelatin will be different, but the correlation of reactivities of oxiranes found from model experiments must remain the same.

Studying the Chemical Modification of Gelatin with Oxirane Compounds

In introducing oxirane compounds with two or more epoxy groups into gelatin emulsion layers cross-linked gelatin structures form, which results in changes in physicomechanical, colloidochemical, membranous and photographic properties of photographic materials. The process of gelatin structuring with the participation of glycidylamines proceeds as a result of the reaction between the oxirane cycle and gelatin amino groups and can be represented by the following scheme:



In order to estimate the hardening action of the synthesized compounds, they were added to 3.5% solution of inert gelatin at pH 7 just before coating. The concentration range was $1.25 \cdot 10^{-5} - 2.00 \cdot 10^{-4}$ moles per 1 g of air-dried gelatin (ADG). Taken as criteria of the structurizing action of the compounds involved were melting temperature and mechanical strength of the swollen gelatin layer. The increase in the number of epoxy groups in the chemical modifier results in the intensification of its hardener action. Thus, tetraglycidylpolymethylendiamines are stronger structurizing agents as compared with triglycidylamine and the reactivity of the latter exceeds that of aliphatic diglycidylamines. With tetraglycidylpolymethylendiamines, the increase in hardening action with the number of methylene groups is observed, which quite agrees with reactivity and basicity of these compounds.

As for aliphatic diglycidylamines, there exists the relationship between the basicity and structurizing action. The experiments show that aromatic diglycidylamines have low reactivity and can only be used as structurizing modifiers together with hardening activators.

Hydrophilic-Hydrophobic Properties of Modified Gelatin Layers

Of great importance for the technology of gelatin emulsion layers is the optimization of their hydrophilic and hydrophobic properties. So it seems important to consider the relation between the hardener structure and hydrophilic and hydrophobic properties of modified gelatin layer.

The character of the gelatin layer surfaces was studied by determining the equilibrium wettening angle. As is evident from the experiments, the introduction of epoxy modifiers into the gelatin layer results, at room temperature, in the hydrophylization of the layer surface, which is accompanied by wetting angle diminishing as compared with unmodified gelatin. In the presence of nonstructurizing modifiers (e.g. monoepoxy compounds), warming up the gelatin layer does not influences the marginal wetting angle, melting point and layer strength. The structurizing modification, which intensively goes on during the warming up the gelatin layer inclusive polyglycidyl hardener, is accompanied by noticable increase in marginal wetting angle as compared with that for non treated material. This suggests a noticeable hydrophobization of gelatin layer surface in the hardening process.

Influence of Color Couplers on Hardening Process

Since the problem of the color coupler influence on the hardening process practically has not been studied, it seemed important to investigate the influence of both hydrophilic nondiffusing and protected color couplers on the chemical modification of gelatin layers by hardeners of glycidylamine series. The experiments were carried out using model gelatin layers, containing $5 \cdot 10^{-4}$ mol./g ADG of the several hydrophilic and protected couplers. Used as hardeners were glycidyl derivatives of aliphatic and aromatic monoamines as well as of alkylendiamines. The data obtained show that the presence of color couplers reduces the hardening process. Hydrophilic nondiffusing color couplers suppress the gelatin structurization to a greater extent as compared with the hydrophobic protected color couplers. The greatest effect is demonstrated by the vellow component of the blue-sensitive layer.

The measurements of hardener distribution between water and dibuthyphtalate (DBPh) have shown that one of the most important factor in the case of protected color couplers is the capture of hardener by the hydrophobic phase of coupler dispersion and the corresponding reduction of its effective concentration in the gelatin layer. The results given in Table 3 show that the extent of tetraglycidylhexamethylendiamine extraction from the aqueous phase is noticeably higher than that of triglycidylamine. The higher the hardener concentration in the organic phase the greater part of it react with color coupler without taking part in gelatin hardening. Investigation of the structurization kinetics reveals that in the presence of protected couplers dispersions the retardation of hardening with tetraglycidylhexamethylendiamine take place in much more extent then with triglycidylamine.

| Table 3. Hardener extraction with DBPh from the | |
|---|--|
| aqueous solution | |

| Hardener | Equilibrium concentration | | k _{distr.} |
|-------------------|---------------------------------|---------|---------------------|
| | of hardener, $mol/l \cdot 10^3$ | | |
| | In water | In DBPh | |
| Triglycidylamine | 10.4 | 5.40 | 0.529 |
| | 9.49 | 4.85 | 0.511 |
| Tetraglycidylhexa | 7.23 | 19.0 | 2.63 |
| methylendiamine | 5.28 | 15.3 | 2.90 |

Gelatin layers hardened in the presence of color couplers are characterized by the higher swelling ability as compared with the reference sample. This effect is more pronounced in case of nondiffusing color couplers.

Thus, it has been found that in the presence of hydrophilic nondiffusing and hydrophobic protected color couplers the hardening process becomes much more complicated. The influence of color couplers is different for different compounds of one and the same series. Hardening effect is determined by both the component nature and the hardener structure and properties. In case of using protected color couplers, the effectiveness of hardening depends, to a great extent, on the hardener distribution between the hydrophilic phase of the gelatin layer and the hydrophobic phase of color coupler dispersion.

Conclusion

A complex physico-chemical and technological study has been done aimed at the improvement of physico-mechanical and photographic properties of black-and-white and color photographic materials using oxirane modifiers.

A new class of chemical modifiers of gelatin emulsion layers – glycidylamines – has been studied.