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Photo-Stabilisation and Photo-Degradation in Organic Coatings Containing A Hindered Amine Light Stabiliser: Part II—Consumption of Hindered Amine

J. L. Gerlock, T. Riley & D. R. Bauer
Research Staff, Ford Motor Company, Dearborn, MI 48121, USA

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ABSTRACT

Gas chromatography has been used to follow the consumption of the hindered amine light stabiliser, bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate (HALS I) in an acrylic/melamine and an acrylic/urethane coating during exposure to ultraviolet (uv) light and humidity. The consumption rate is found to be a function of coating composition, exposure light intensity and humidity. In all cases, the rate of consumption is less than the photo-initiation rate of free radicals but greater than the net formation rate of nitroxide during the early stages of exposure. HALS I consumption in the urethane coating is found to be independent of humidity. HALS I consumption in the acrylic/melamine coating decreases with increasing humidity during exposure. In contrast, it was found in the previous paper that the net nitroxide formation rate increased with increasing humidity. This behavior can be accounted for by regeneration of hindered amine from nitroxide in the acrylic/melamine coating exposed under humid conditions. Another unexpected reaction observed in the acrylic/melamine coating is the conversion of HALS I $>N{-}H$ *groups to* $>N{-}CH_3$ *groups. These reactions are thought to involve formaldehyde which is released in the acrylic/melamine coating during cure and during exposure as a result of acrylic/melamine crosslink hydrolysis.*

INTRODUCTION

Hindered amine light stabilisers such as bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate (HALS I) can be oxidised to nitroxides by oxidants

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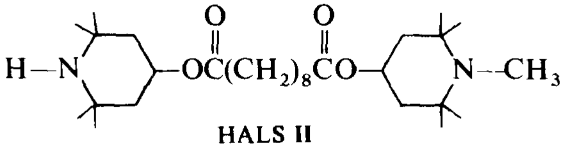
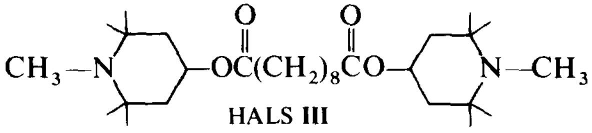
produced in polymers during photolysis. This and the subsequent reactions of nitroxides and their byproducts have been described by several authors[1-4] and are summarised in Fig. 1 of the previous paper.[5] Nitroxides scavenge free radicals produced in the polymer on photolysis to yield aminoethers. Aminoethers, in turn, can react with polymer-based oxidants to regenerate nitroxide. The variation in nitroxide concentration with time is determined by the difference between nitroxide formation and consumption rates. It has been found that in acrylic/melamine coatings doped with HALS I, the nitroxide concentration rises to a maximum and then slowly decreases.[5-7] The slow decrease is apparently due to conversion of nitroxide or its precursors to non-nitroxide recyclable forms. The net nitroxide formation rate is constant in time over the early stages of exposure. In the previous paper,[5] the net nitroxide formation rates (along with other parameters) have been measured for an acrylic/melamine and an acrylic/urethane coating as a function of ultraviolet (uv) light intensity and humidity. It was found that the net nitroxide formation rate was much larger in the acrylic/melamine coating than it was in the acrylic/urethane coating and that in the acrylic/melamine coating, the net nitroxide formation rate increased with increasing humidity of exposure. It was suggested that formaldehyde produced during cure and as a byproduct of acrylic/melamine crosslink hydrolysis could account for these effects. Aldehyde based peracids readily oxidise secondary amines to nitroxides.

Since the nitroxide concentration observed only reflects the balance between nitroxide formation and consumption, these measurements by themselves cannot provide much information concerning the flux of the stabilisation reactions. More information can be obtained by also measuring the consumption rate of HALS I during exposure. In this paper, measurements of the concentration of HALS I as a function of exposure time, light intensity and humidity are reported for both the acrylic/urethane coating and the acrylic/melamine coating of the previous paper.[5] HALS I was determined by gas chromatographic assay of methylene chloride extracts of coatings exposed for various periods of time. In addition to providing a convenient monitor of the HALS I concentration, the gas chromatographic traces also revealed the formation of two different HALS additives (II and III) from HALS I. Mechanisms for the formation of these species are presented, along with a discussion of the relationship between the net nitroxide formation rate and the initial HALS I consumption rate observed in these coatings.



HALS II



HALS III

EXPERIMENTAL

The two coatings (the acrylic/melamine and the acrylic/urethane) are identical to those used in the previous paper,[5] as were the techniques of sample preparation. Known amounts of coating, exposed for given lengths of time, were placed in flasks containing known amounts of methylene chloride and allowed to stand overnight. After the soluble portion was extracted, a known amount of di (2-ethylhexyl) sebacate (DEHS) was added to the solution as an internal standard. Approximately 5 microlitres of the mixture were then injected into a Perkin Elmer Sigma 2 gas chromatograph equipped with a Sigma 10 data station. A 6 ft 100–120 mesh Gas Chrom Q with 3% OV-17 column was used. The initial oven temperature was 220 °C, rising at a rate of 10 °C per minute to 290 °C. A typical chromatograph from extracts of the acrylic/melamine coating is shown in Fig. 1. The retention time and sensitivity factor of HALS I was determined by injecting known amounts of HALS I and DEHS. HALS II and HALS III assignments were made by gc-ms. It was assumed that the sensitivity factors of HALS II and HALS III were identical to HALS I. The measured concentrations of HALS I were reproducible to better than ±5–10%. Aminoethers could not be detected by this assay.

RESULTS

Acrylic/urethane coating

The concentration of HALS I as a function of exposure time is shown in Fig. 2 for the acrylic/urethane coating exposed at dew points of −40 °C

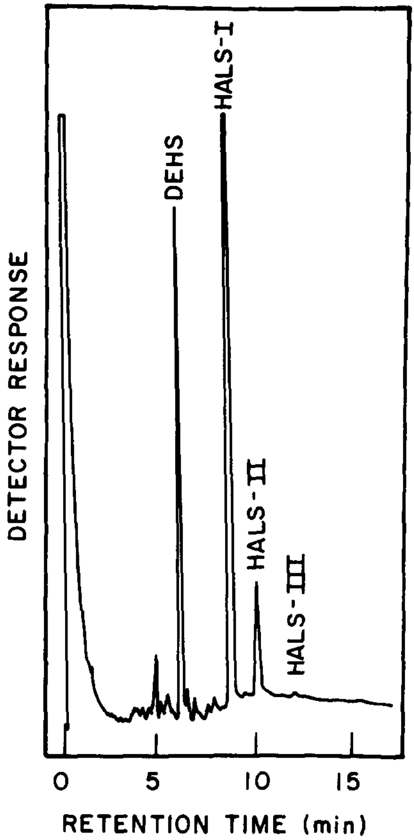


Fig. 1. FID detector response versus retention time for extract of acrylic/melamine coating.

and 25 °C. Within experimental error, the consumption of HALS I in the acrylic/urethane coating is independent of humidity. Not all of the HALS I added to the coating is recovered after cure. The theoretical amount of HALS I extractable from the coating is $4{\cdot}1 \times 10^{-5}$ mole/g. As can be seen from Fig. 2, only about 70 % of the original HALS I is extractable from the coating after cure. It is not clear whether the missing HALS I is lost from the coating during cure or whether it is simply not extractable. It should be noted that all of the HALS I can be recovered from uncured coatings. No measurable levels of HALS II or HALS III were detected in the acrylic/urethane coating either after cure or after exposure.

The consumption of HALS I is roughly linear with time over the first 25 % of the consumption so that the initial rate of consumption of HALS

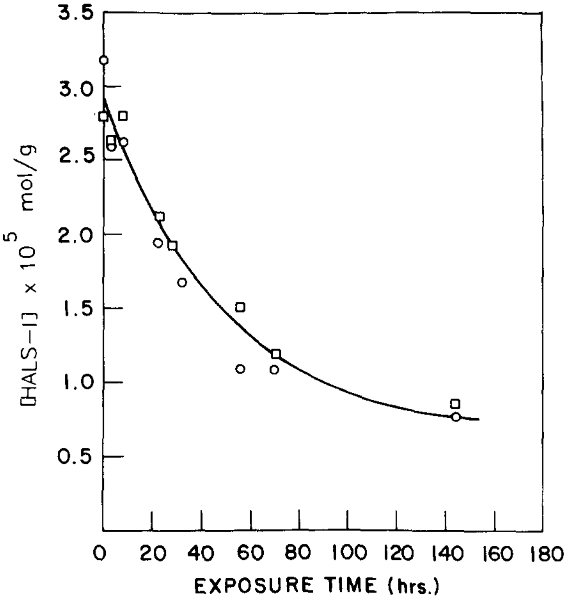


Fig. 2. HALS I concentration versus time for the acrylic/urethane coating exposed at dew points of −40 °C (○) and 25 °C (□). The photo-initiation rate of free radicals was 12×10^{-8} moles/g, min.

I can be determined to within ± 10 %. Values of the consumption rate of HALS I are given in Table 1. The initial rate of consumption of HALS I is identical to the initial rate of consumption of $>$NH functionality since, initially, for every mole of $>$NH consumed, a mole of HALS I is lost. At longer exposure times the relationship between the concentration of HALS

TABLE 1
Hindered Amine Consumption Rates

Coating	*Dew point (°C)*	W_i^a	$-d[>NH]/dt_i^a$	$d[>NO\cdot]/dt_i^a$
Acrylic/urethane	−40	12·0	0·78	0·012
Acrylic/urethane	25	12·0	0·78	0·016
Acrylic/melamine	−40	12·0	1·35	0·09
Acrylic/melamine	−40	7·0	0·95	0·09
Acrylic/melamine	−40	1·4	0·55	0·07
Acrylic/melamine	25	12·0	0·59	0·24

[a] $\times 10^8$ mole/g, min. Nitroxide formation data from reference 5.

I in the film and the concentration of total $>$NH in the film is more complex since each HALS I contains two $>$NH groups. It can be shown that the concentration of $>$NH groups is related to the concentration of HALS I by the following expression:

$$[>\mathrm{NH}](t) = 2[\mathrm{HALS\ I}](\mathrm{O}) \times \sqrt{[\mathrm{HALS\ I}](t)/[\mathrm{HALS\ I}](\mathrm{O})} \qquad (1)$$

Although the gas chromatographic technique does not yield information on the nature and concentration of NOY species directly, it is possible to infer the total concentration of NOY and NOH species over the initial part of the exposure (before substantial amounts of total stabiliser are lost) simply by mass balance:

$$[>\mathrm{NOY}](t) + [>\mathrm{NOH}](t) = [>\mathrm{NH}](\mathrm{O}) - [>\mathrm{NH}](t) - [>\mathrm{NO}\cdot](t) \qquad (2)$$

As can be seen from Table 1, the initial rate of consumption of $>$NH is much greater than the rate of formation of nitroxide. Also, the nitroxide level in this coating continues to increase even though a substantial fraction of HALS I has been consumed by 140 hours' exposure. The consumption curves approximate, but do not exactly follow, first order kinetics over the entire exposure time.

Acrylic/melamine coating

The consumption of HALS I in the acrylic/melamine coating exposed at a dew point of −40 °C is shown in Fig. 3. The consumption of HALS I in the same coating exposed at a dew point of 25 °C is shown in Fig. 4. Again, only about 65 % of the original hindered amine is extractable after cure. As shown in Table 1, the initial rate of loss of HALS I from the acrylic/melamine coating exposed at a dew point of −40 °C is roughly twice as large as that from the acrylic/urethane coating. The initial rate of HALS I consumption is roughly proportional to the square root of the light intensity. Despite the fact that the net nitroxide formation rate in the HALS I doped acrylic/melamine coating increases with increasing humidity, the initial consumption rate of hindered amine actually decreases with increasing humidity. In addition, the shape of the consumption curve is qualitatively different at long exposure times. The curve for the −40 °C dew point exposure is roughly first order in HALS I concentration while the curve at 25 °C dew point deviates strongly from first order kinetics. From Fig. 4 and eqn (1) it can be seen that the level

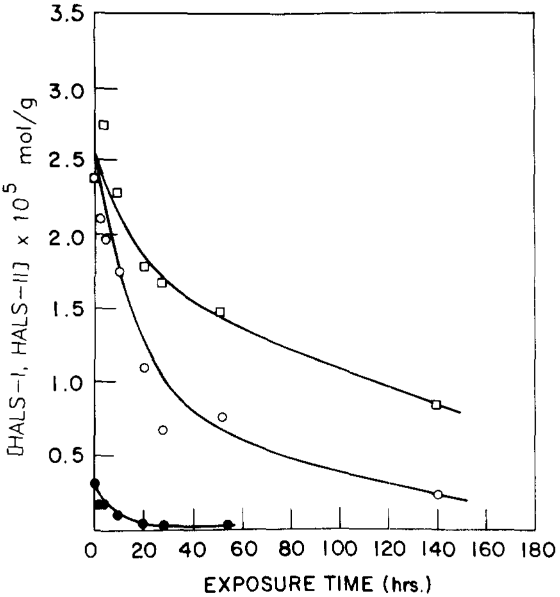


Fig. 3. HALS I and HALS II concentration versus time for the acrylic/melamine coating exposed at a dew point of −40°C. The open symbols denote HALS I and the closed symbols, HALS II. The photo-initiation rates were 12×10^{-8} moles/g, min (○) and $1{\cdot}4 \times 10^{-8}$ moles/g, min (□).

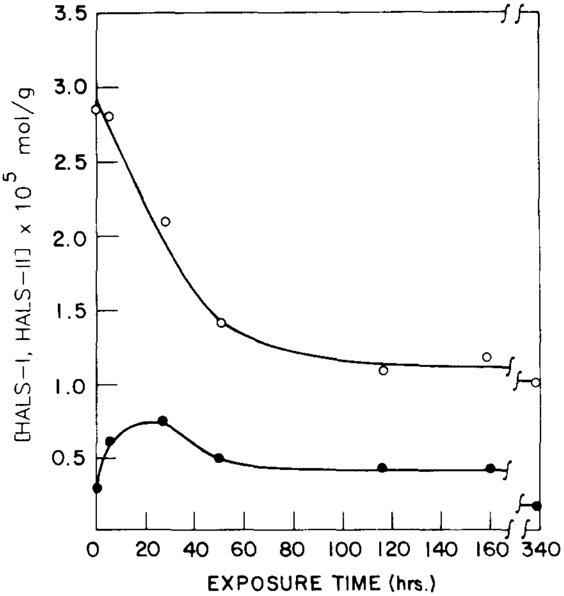


Fig. 4. HALS I and HALS II concentration versus time for the acrylic/melamine coating exposed at a dew point of 25°C. The open symbols denote HALS I and the closed symbols, HALS II.

of >NH groups observed in the coating drops by 40 % over the first 120 h of exposure, then remains almost constant for the next 200 h.

In addition to observing HALS I, two other hindered amines are extractable from the acrylic/melamine coating after cure (II and III). The level of HALS II is roughly 13 % of the total HALS extracted after cure while the level of HALS III is less than 1 %. The variation in concentration of HALS II with exposure time is a strong function of the humidity of the exposure. At −40 °C dew point, HALS II decreases rapidly with exposure. At 25 °C dew point, on the other hand, the concentration of HALS II initially rises, then slowly decreases. The concentration of HALS III is so low that it is difficult to quantify. Qualitatively, it behaves in a fashion similar to HALS II.

DISCUSSION

In all cases, the initial rate of consumption of NH functionality is substantially less than the photo-initiation rate but substantially greater than the net nitroxide formation rate at short exposure times. Following Fig. 1 of the previous paper, the rate of consumption of amine and the rate of formation of nitroxide are related by the following:

$$\mathrm{d}[>\mathrm{NH}]/\mathrm{d}t = -k[\mathrm{YOO}\cdot][>\mathrm{NH}] \tag{3}$$

$$\mathrm{d}[>\mathrm{NO}\cdot]/\mathrm{d}t = k[\mathrm{YOO}\cdot][>\mathrm{NH}] - k'[\mathrm{Y}\cdot][>\mathrm{NO}\cdot] \tag{4}$$

Thus in the limit $[>\mathrm{NO}\cdot] \rightarrow 0$, the initial nitroxide formation rate should be equal in magnitude to the initial hindered amine consumption rate. In fact, as shown in Table 1, the net nitroxide formation rate is smaller than the initial hindered amine consumption rate by a factor of 2–50, depending on the coating and exposure condition. There are two possible explanations for this difference. First, some of the >NH groups may be oxidised directly to aminoether groups rather than nitroxide. To our knowledge, such a reaction has not been reported. Secondly, it should be recalled that the nitroxide concentration after cure, but before exposure, is small but not zero. It is possible that the nitroxide scavenging rate constant, k', is large enough so that the scavenging rate is comparable with the nitroxide formation rate even at very low nitroxide levels. This possibility will be analysed in detail in the final paper in this series.[8]

The consumption of HALS I in the acrylic/melamine coating under humid exposure conditions is surprising. The initial rate of consumption is smaller in the 25 °C dew point exposure than it was in the −40 °C dew point exposure even though the net nitroxide formation rate and the photo-oxidation rate are larger.[9] Also, the rate of consumption of >NH functionality drops nearly to zero at a point where only 40 % of the >NH functionality has been consumed. This suggests that there exists a mechanism to regenerate >NH functionality from nitroxide or other species. A clue as to the nature of the mechanism is given by the fact that this behavior is only observed to a measurable extent in the acrylic/melamine coating during humid exposure. It has already been suggested that formaldehyde released as a byproduct of hydrolysis influences the free radical oxidation kinetics and the rate of conversion of >NH groups to >NO· groups via peracid chemistry. As shown in Fig. 5, reasonable schemes regenerating >NH groups from >NO· groups can also be written involving formaldehyde byproducts.

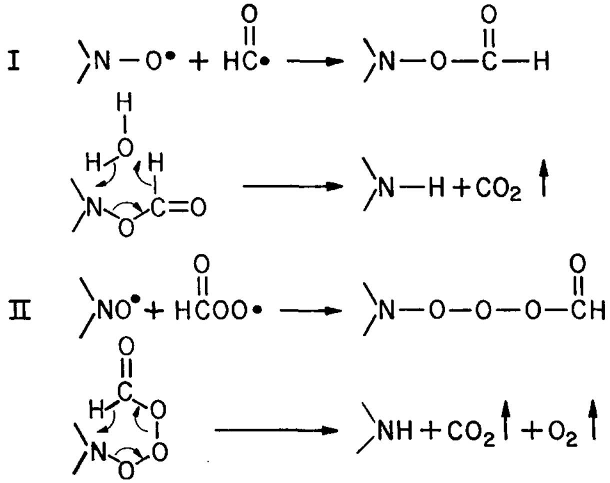


Fig. 5. Tentative mechanisms for the regeneration of >NH functionality from >NO· functionality.

The first mechanism requires the presence of water as a proton transfer agent. It is likely that small amounts of formaldehyde are released in the acrylic/melamine coating even during dry exposure through deformylation of residual methylol groups. This may account for the difference in HALS I consumption between the acrylic/urethane coating and the acrylic/melamine coating exposed at −40 °C dew point. The fact that >NH group regeneration is only observed under humid conditions seems to argue for the first mechanism of Fig. 5. However, in the absence of direct chemical evidence on model systems both mechanisms must remain tentative.

Formaldehyde is also most probably responsible for the generation of HALS II and HALS III in the acrylic/melamine coatings. Formaldehyde is a known methylating agent for secondary amines.[10] The relative concentrations of HALS II and HALS III are consistent with a random stepwise methylation of >NH groups on HALS I. The behavior of the HALS II level with exposure is also consistent with this mechanism. It is known that $>NCH_3$ groups are rapidly converted to >NH groups during photo-oxidation.[11] During exposure at −40 °C dew point, the level of formaldehyde release is apparently too small to regenerate many $>NCH_3$ groups and the level of HALS II and HALS III drops rapidly. During humid exposure, on the other hand, there is sufficient formaldehyde released to maintain a substantial amount of $>NCH_3$ functionality. In fact, the ratio of $>NCH_3$ to >NH functionality increases from 6% just after cure to roughly 17% after about 20 hours' exposure. This rate remains roughly constant over the first 200 hours' exposure. The methylation reaction and the amine regeneration reaction have not been previously observed in studies of HALS chemistry in either model compounds or polymers such as polypropylene.[1–4] Peracid chemistry has been invoked to explain rapid oxidation of amine to nitroxide.[12] The chemistry of HALS I in acrylic/melamine coatings, as summarized in Fig. 6, is clearly different from that of either polypropylene or the acrylic/urethane coating studied here. In view of these differences and in view of the differences in oxidation chemistry between the acrylic coatings and polypropylene,[7] it should not be surprising that the behavior and effectiveness of HALS additives in acrylic coatings—and particularly melamine crosslinked coatings—are

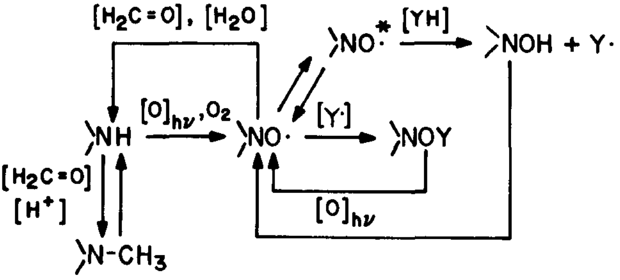


Fig. 6. Hindered amine light stabiliser chemistry in acrylic/melamine coatings.

vastly different from that in polypropylene or polyethylene. Significant differences should also be expected between melamine and urethane crosslinked coatings. The data in this and the previous paper[5] are used in the final paper in this series[8] to attempt to quantify these differences.

CONCLUSION

Gas chromatography has been used to follow the concentration of HALS I remaining in acrylic/melamine and acrylic/urethane coatings as a function of exposure time and exposure condition. The conversion of HALS $>$NH functionality to $>$NCH$_3$ functionality was also studied. The HALS I consumption rate is contrasted with the net nitroxide formation rate for identical coatings exposed to the same conditions. In all cases the rate of consumption of amine is greater than the rate of formation of nitroxide but smaller than the photo-initiation rate. The rate of consumption of hindered amine is roughly proportional to the square root of the light intensity. The rate of consumption in the acrylic/urethane coating was found to be independent of humidity. In contrast, in the acrylic/melamine coating, the HALS I consumption rate decreases, while the net nitroxide formation rate increases, with increasing humidity. Regeneration of hindered amine from nitroxide, possibly via formaldehyde-based radicals, was proposed to account for this effect. The chemistry of stabilisation by HALS is complex and depends strongly on the degradation chemistry of the polymer to which they are added. Thus, the same HALS compound can behave quite differently in different polymers and under different exposure conditions. Measurements of just the nitroxide concentration or the HALS I concentration are insufficient by themselves to understand the stabilisation chemistry. Even together, other ancillary data (e.g. photo-initiation rates and kinetic chain lengths) are required before the stabilisation chemistry can be understood. The data of this and the previous paper, together with this ancillary data, are used to derive values for the various stabilisation rate constants in the final paper of this series.

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REFERENCES

1. D. J. Carlsson, A. Garton and D. M. Wiles, in, *Developments in polymer stabilization—1.* (G. Scott (Ed.)), Applied Science Publishers, London, 219 (1979).
2. V. Ya. Shlyapintokh and V. B. Ivanov, in, *Developments in polymer stabilization—5.* (G. Scott (Ed.)), Applied Science Publishers, London, 41 (1982).
3. M. Dagonneau, V. B. Ivanov, E. G. Rozantsev, V. D. Sholle and E. G. Kagan, *Rev. Macromol. Chem. Phys.*, **C22**, 169 (1983).
4. G. Scott, *J. Photochem.*, **25**, 83 (1984).
5. J. L. Gerlock, D. R. Bauer and L. M. Briggs, *Poly. Deg. and Stab.*, **14**, 53 (1986).
6. J. L. Gerlock, H. van Oene and D. R. Bauer, *Euro. Polym. J.*, **19**, 11 (1983).
7. J. L. Gerlock, D. R. Bauer and L. M. Briggs, *Polymer Preprints*, **25** (1), 10 (1984).
8. D. R. Bauer and J. L. Gerlock, *Poly. Deg. and Stab.*, **14**, 97 (1986).
9. J. L. Gerlock, D. R. Bauer and L. M. Briggs, *Polym. Mat. Sci. Eng.*, **52**, 503, (1985).
10. M. L. Moore, *Organic reactions* (R. Adams (Ed.)), John Wiley and Sons, Inc., New York, Vol. 5, Chapter 7, 307 (1949).
11. D. J. Carlsson and D. M. Wiles, *Polymer Preprints*, **25** (1), 24 (1984).
12. B. N. Felder, *Polymer Preprints*, **25** (1), 26 (1984).