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INFLUENCE OF AROMATIC NITRO COMPOUNDS ON RETARDING OF RADICAL POLYMERIZATION. PART II.* INFLUENCE OF SOME DISUBSTITUTED DERIVATIVES OF BENZENE

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Zbadano wpływ kilkudziesięciu nitrozwiązków aromatycznych na kopolimeryzację nienasyconej żywicy poliestrowej "Polimal 109". Stwierdzono, że opóźnienie tej reakcji zależy od wzajemnego położenia grup funkcyjnych. Szczególnie aktywne okazały się związki *o*-mononitropochodne.

Исследовано влияние нескольких десятков ароматических нитросоединений на сополимеризацию непредельной полиэфирной смолы „Полималь 109". Найдено, что опаздывающее действие нитросоединений зависит от положения функциональных групп. Особенно активными оказались *орто*-нитросоединения.

The reaction of a few dozens of aromatic nitro compounds was examined on copolymerization of unsaturated polyester resin "Polimal 109". It has been found that the retarding of radical polymerization depends on the position of substituents. *Ortho* mononitro compounds are particularly active.

The mechanism of the retarding action of aromatic nitro compounds on radical polymerization was the subject matter of a number of papers which have given so far controversial results. These papers have been reviewed by us in our previous paper ¹⁾, in which we suggested a novel mechanism of retarding the polymerization. According to our suggestion it consists in a migration of the hydrogen atom from the polymerizing chain to the nitro group and the formation of an adduct. The nitro compound is subsequently regenerated from the latter.

The aim of the present paper has been to elucidate the influence of various functional groups and of their position on the activity of the nitro group retarding the polymerization.

EXPERIMENTAL

We applied the method of investigation as presented previously ¹⁾.

The unsaturated polyester resin "Polimal 109" served as a standard polymerizable medium. In this medium we examined the peak exotherm temperature (t_m), the gel time ($\tau_{ż}$), the cure time (τ_u) and the maximum rate of the temperature increase (v_m). These four parameters changed under the influence of added nitro compounds. The accuracy of reading of these parameters was as follows: t_m — ±0.5°C; v_m — ±4°C/min; $\tau_{ż}$ and τ_u — ±2.5 s.

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* Part I: Buźniak J., Urbański T., *Polimery*, **15**, 333 (1970).

The differences between the parameters of a standard resin and the parameters of the same resin with nitro compounds are given in Tables 1 and 2 (Δt_m, Δv_m, $\Delta \tau_ż$, and $\Delta \tau_u$).

The copolymerization was initiated by benzoyl peroxide in form of a paste in dibutyl phthalate in the ratio 50/50. The initiator was added in an amount producing the drop of the peak exotherm temperature by 12°C per each 1 g of added nitrobenzene to 100 g standard resin [1]).

High purity nitrobenzene (m.p. 5.1—5.5°C, n^D_{20} — 1.5527) was used as a standard nitro compound.

The following nitro compounds were investigated: *o*-, *m*- and *p*-mononitro derivatives of toluene, diphenyl, benzyl alcohol, benzaldehyde, benzoic acid, chlorobenzene, bromobenzene, phenol, anisole, aniline, N-methylaniline, N,N-dimethylaniline, acetanilide, and N-methylacetanilide as well as *o*-, *m*-, and *p*-dinitrobenzene. Salicylaldehyde was also investigated for comparative purposes.

The examined compounds, if not commercially available, were obtained by methods described in the literature. The m.p.'s (as a criterion of purity) have been in agreement with the literature. All nitro compounds were added in concentration 2×10^{-5} mole per 1 g standard resin or 2×10^{-5} gram-equivalent in case of dinitro compounds.

o-Nitrophenol and *o*-nitroacetanilide were examined within the wide range of concentration as in the case of nitrobenzene [1]), because these compounds behaved in a different way as compared with the other ones.

It is necessary to mention that the non-nitrated substances — the mother compounds of the examined nitro derivatives — were investigated in our previous paper [1]).

RESULTS AND DISCUSSION

Our results are given in Tables 1 and 2. The actions of some nitro compounds are shown in Figs 1—7. The variations of examined parameters against the concentration of *o*-nitrophenol and *o*-nitroacetanilide in the standard resin are shown in Figs 8—10. The comparison of the action of *m*-nitro compounds with that of *p*-nitro compounds is given in Figs 11 and 12.

The results in Table 1 and Figs 1—6 show clearly that *ortho* mono-

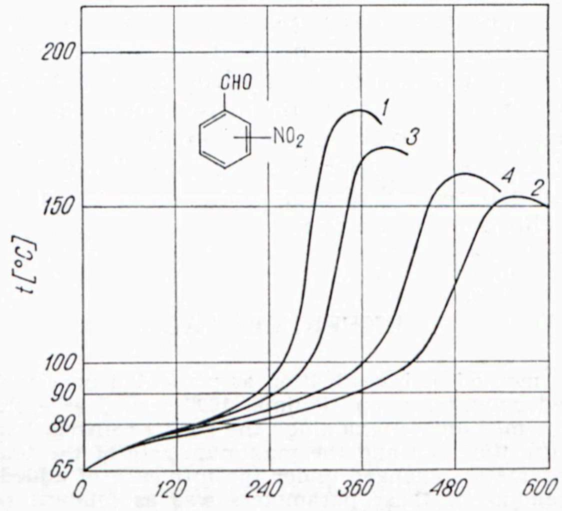


Fig. 1. Trend of copolymerization of standard polyester resin (*1*) and the same resin with mono nitro derivatives of benzaldehyde *ortho* (*2*), *meta* (*3*), and *para* (*4*) in concentration 2×10^{-5} mole per 1 g resin

Table 1

Variation of parameters t_m, v_m, $\tau_{\dot{z}}$, and τ_u of standard resin under influence of mononitro derivatives of benzene at constant concentration

Standard compound — nitrobenzene: $\Delta t_m = 10$; $\Delta v_m = 16$; $\Delta \tau_{\dot{z}} = 15$; $\Delta \tau_u = 25$

No	Examined compounds[a)] 2×10⁻⁵ mole per 1 g standard rezin	*o*-derivatives				*m*-derivatives				*p*-derivatives				Figure
		Δt_m °C	Δv_m °C/min	$\Delta \tau_{\dot{z}}$ s	$\Delta \tau_u$ s	Δt_m °C	Δv_m °C/min	$\Delta \tau_{\dot{z}}$ s	$\Delta \tau_u$ s	Δt_m °C	Δv_m °C/min	$\Delta \tau_{\dot{z}}$ s	$\Delta \tau_u$ s	
1	nitrotoluene	12	28	32.5	52.5	8.5	4	10.5	12.5	9	4	5	7.5	—
2	nitrodiphenyl	12	28	17.5	32.5	9	12	17.5	27.5	11.5	20	0	2.5	—
3	nitrobenzyl alcohol	14	36	27.5	47.5	7.5	8	10	12.5	8	20	2.5	5	—
4	nitrobenzaldehyde	28	76	125	210	12	40	25	35	21	66	77.5	140	1
5	nitrobenzoic acid	15	36	90	115	12	24	45	55	13	36	55	82.5	—
6	chloronitrobenzene	27.5	64	107.5	182.5	18	32	20	40	16	24	47.5	65	—
7	bromonitrobenzene	31	68	107.5	205	17	36	40	67.5	14.5	32	32.5	50	—
8	nitrophenol	92	96	—	1300[b)]	10	22	17.5	30	13.5	20	17.5	32.5	3
9	nitroanisole	16.5	28	35	67.5	12.5	20	25	37.5	12	20	15	20	4
10	nitro-N,N-dimethylaniline	30.5	84	122.5[c)]	252.5[c)]	19	32	−72.5[d)]	−85[d)]	17.5	38	−10	0	2
11	nitroacetanilide	86	94	1100[b)]	1100[b)]	12	20	7.5	7.5	13	8	12.5	12.5	5
12	nitro-N-methylacetanilide	18.5	44	17.5	50	13.5	32	7.5	15	12	24	12.5	17.5	6
13	salicylaldehyde	1	4	15	20	—	—	—	—	—	—	—	—	—

a Nitroaniline and nitro-N-methylaniline gave non-reproducible results.

b Results of an insufficient accuracy because of a low peak exotherm temperature (t_m).

c Approximate results due to a tendency to increase the values of gel time ($\tau_{\dot{z}}$) and cure time (τ_u) with extension of induction period of standard resin.

d Approximate results because of tendency to decrease the values of gel time ($\tau_{\dot{z}}$) and cure time (τ_u) with extension of induction period of standard resin (acceleration of radical polymerization).

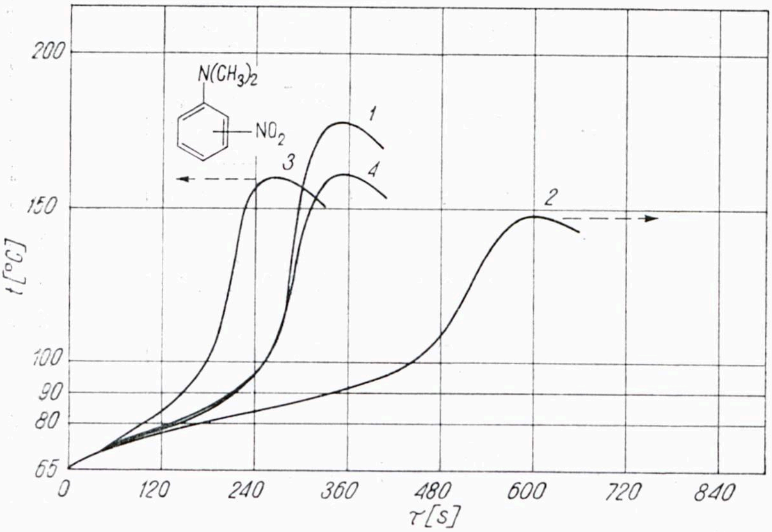


Fig. 2. Trend of copolymerization of standard polyester resin (*1*) and the same resin with mono nitro derivatives of N,N-dimethylaniline *ortho* (*2*), *meta* (*3*), and *para* (*4*) in concentration 2×10^{-5} mole per 1 g resin

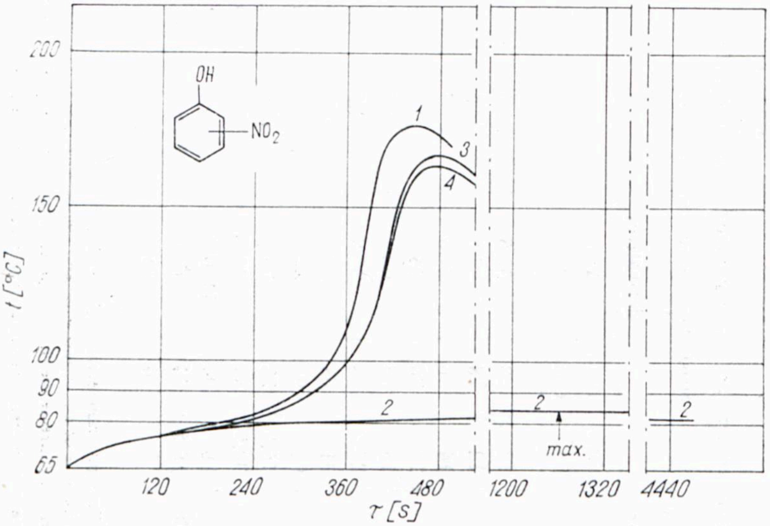


Fig. 3. Trend of copolymerization of standard polyester resin (*1*) and the same resin with mono nitro derivatives of phenol *ortho* (*2*), *meta* (*3*), and *para* (*4*) in concentration 2×10^{-5} mole per 1 g resin

nitro compounds are the most active retardants of the radical polymerization. In the instance of the derivatives of nitrophenol this was noticed previously [2,3].

In case of derivatives of aniline and N-methylaniline the above regularity was not found, because the results were not reproducible. We suppose that this was caused by the sensibility of these compounds to the oxidizing action of the initiator.

We also suppose that in case of *o*- and *m*-nitro-N,N-dimethylaniline the oxidizing action of the initiator accounts for the instability of the

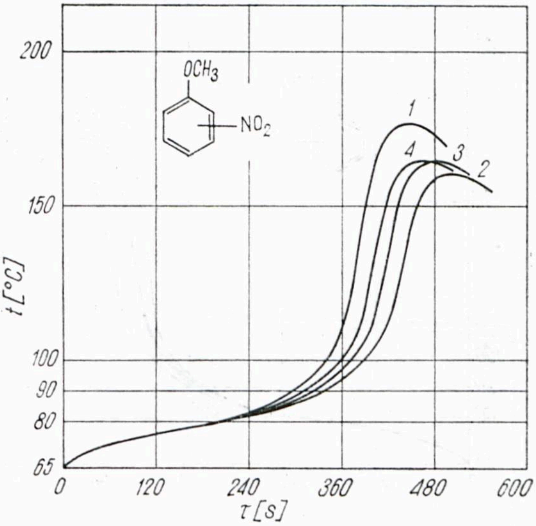


Fig. 4. Trend of copolymerization of standard polyester resin (*1*) and the same resin with mono nitro derivatives of anisole *ortho* (*2*), *meta* (*3*), and *para* (*4*) in concentration 2×10^{-5} mole per 1 g resin

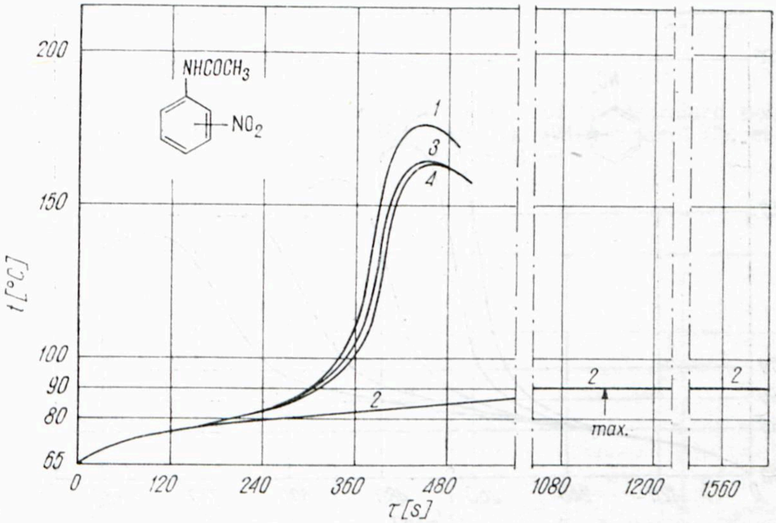


Fig. 5. Trend of copolymerization of standard polyester resin (*1*) and the same resin with mono nitro derivatives of acetanilide *ortho* (*2*), *meta* (*3*), and *para* (*4*) in concentration 2×10^{-5} mole per 1 g resin

parameters $\tau_{ż}$ and τ_u. This instability is dependent upon the induction period of standard resin. The course of the variation was marked with arrows in Fig. 2.

It is necessary to emphasize that in the course of examining other nitro compounds, in particular nitrobenzene, we observed no instability of the parameters $\tau_{ż}$ and τ_u.

In the case of nitro derivatives of N,N-dimethylaniline we also observed that *m*-isomer accelerated, *o*-isomer retarded and *p*-isomer behaved

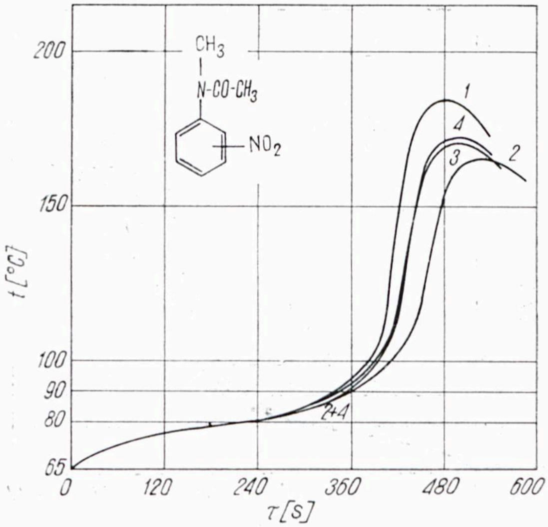


Fig. 6. Trend of copolymerization of standard polyester resin (*1*), and the same resin with mono nitro derivatives of N-methylacetanilide *ortho* (*2*), *meta* (*3*), and *para* (*4*) in concentration 2×10^{-5} mole per 1 g resin

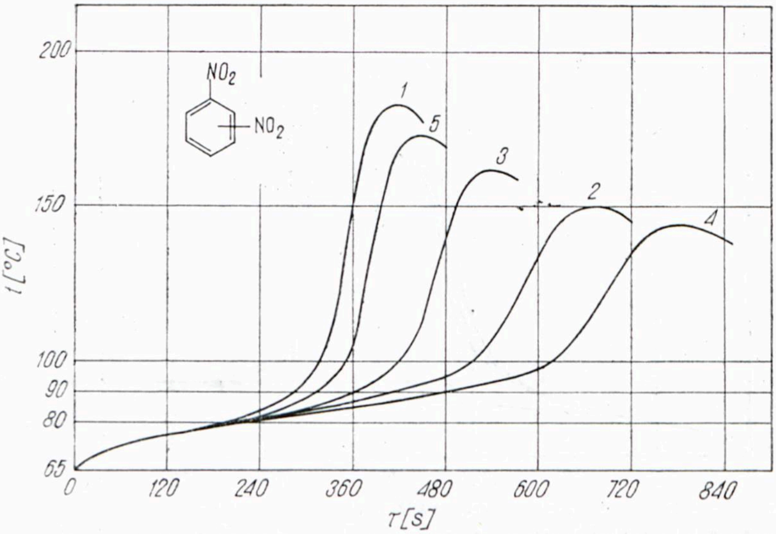


Fig. 7. Trend of copolymerization of standard polyester resin (*1*) and the same resin with isomers dinitrobenzene *ortho* (*2*), *meta* (*3*), and *para* (*4*) as well as nitrobenzene (*5*) in concentration 2×10^{-5} gram-equivalent nitro groups per 1 g resin

neither retarding nor accelerating the radical polymerization (Fig. 2). However, these compounds cause a decrease in the values t_m and v_m like all other nitro compounds.

It is necessary to mention that *m*-nitro-N,N-dimethylaniline is the only nitro compound, examined by us, which accelerates the radical polymerization. In the future the investigation of the properties of nitro derivatives of N,N-dimethylaniline will be continued.

As may be seen from Table 1 and Figs 3—5 *o*-nitrophenol and *o*-nitroacetanilide show a particularly high activity in retarding action of the radical polymerization. This induced us to examine thoroughly the mentioned nitro compounds within the wide range of concentration in the standard resin (Figs 8—10).

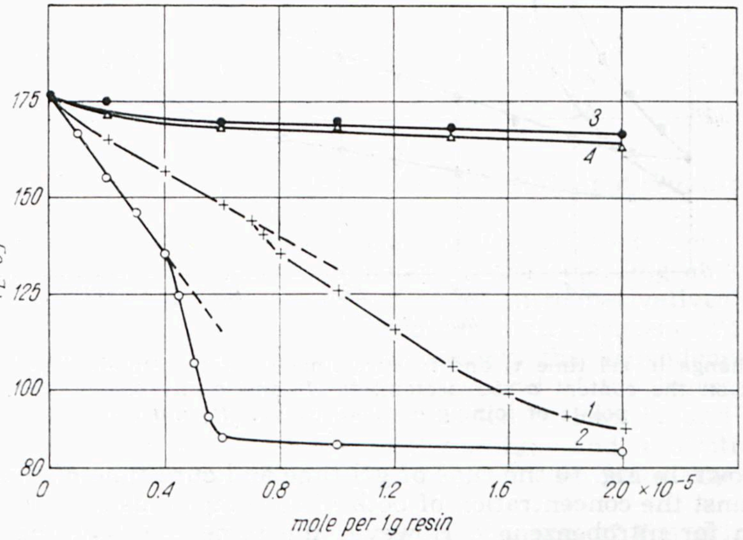


Fig. 8. Change in peak exotherm temperature (t_m) of the standard polyester resin depending on the content of *o*-nitroacetanilide (*1*), *o*-nitrophenol (*2*), *m*-nitrophenol (*3*), and *p*-nitrophenol (*4*)

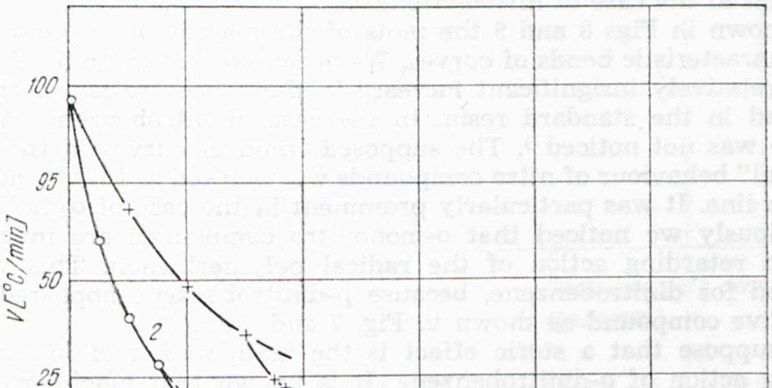


Fig. 9. Change in maximum rate of temperature increase (v_m) of the standard polyester depending on the content *o*-nitroacetanilide (*1*) and *o*-nitrophenol (*2*)

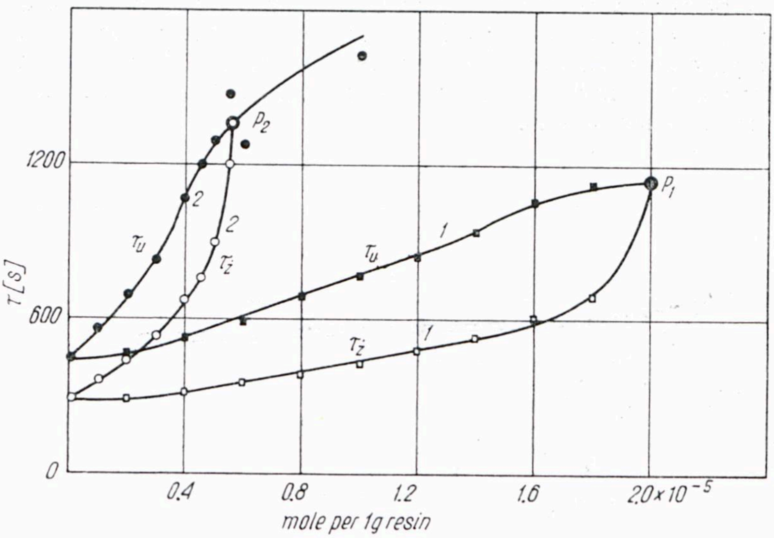


Fig. 10. Change in gel time $\tau_{\dot{z}}$ and in cure time τ_u of the standard polyester resin depending on the content *o*-nitroacetanilide (*1*) and *o*-nitrophenol (*2*) with visible points of joining of these curves (P_1 and P_2)

As shown in Fig. 10 the runs of gel time and cure time of the standard resin against the concentration of both nitro compounds are similar to the same run for nitrobenzene [1]. However the same effect of the retarding action of the radical polymerization is caused by much lower concentration of *o*-nitrophenol or *o*-nitroacetanilide. As an example it may be given that the characteristic point of the joining of the curves $\tau_{\dot{z}}$ and τ_u (points P_1 and P_2 in Fig. 10) appears in the case of *o*-nitrophenol for the concentration about 230 times lower and of *o*-nitroacetanilide about 60 times lower that in the case of nitrobenzene [1].

As shown in Figs 8 and 9 the plots of the magnitudes t_m and v_m give the uncharacteristic bends of curves. We observed that these bends appear after a relatively insignificant increase in the concentration of the nitro compound in the standard resin. In the case of nitrobenzene this bend of curve was not noticed [1]. The supposed trend of curves in the case of a "normal" behaviour of nitro compounds was marked in Figs 8 and 9 with a broken line. It was particularly prominent in the case of *o*-nitrophenol.

Previously we noticed that *o*-mononitro compounds are much more active in retarding action of the radical polymerization. This was not confirmed for dinitrobenzene, because *p*-dinitrobenzene appeared to the most active compound as shown in Fig. 7 and Table 2.

We suppose that a steric effect is the main reason of lowering the retarding action of *o*-dinitrobenzene. It is known that neighboring nitro groups have a restricted rotation by reason of their magnitude. It may cause a reduced activity of nitro groups in a polymerizable medium, because these groups are not placed in coplanar position.

It is interesting that the behavior of isomeric dinitrobenzenes is different in media different from ours and under other conditions. A short time ago Mondvai and coworkers [4] showed that *o*-dinitrobenzene was a stronger retarder than other isomers in a radical polymerization of methyl methacrylate. On the other hand, in case of polymerization of

Table 2

Variation of parameters t_m, v_m, $\tau_ż$, and τ_u of standard resin under influence of isomers of dinitrobenzene at constant concentration (Figure 7)

No	Examined compounds (2×10^{-5} gram-equivalent of nitro group per 1 g standard resin)	Δt_m °C	Δv_m °C/min	$\Delta \tau_ż$ s	$\Delta \tau_u$ s
1	*o*-dinitrobenzene	33	70	140	255
2	*m*-dinitrobenzene	21,5	48	75	130
3	*p*-dinitrobenzene	39	76	200	360
4	nitrobenzene (standard compound)	10	16	15	25

allyl acetate Hammond and Bartlett[5)] found that *o*-dinitrobenzene was a weaker retarder than other isomers.

It was also found in our investigations that neither *meta* nor *para* nitro compounds showed a predominance in the retarding action of the radical polymerization with an exception of nitro derivatives of benzaldehyde, N,N-dimethylaniline and isomers of dinitrobenzene. To compare the properties of *meta* and *para* nitro isomers the dependences of the decrease in the peak exotherm temperature and of the increase in the cure time by mentioned isomers are presented in Figs 11 and 12. Only *p*-nitrobenzaldehyde, *p*-nitro-N,N-dimethylaniline and *p*-dinitrobenzene act stronger that their *m*-isomers. This effect is seen from Figs 1, 2, and 7, too.

It is necessary to mention that the comparison of the gel time ($\tau_ż$) and of the maximum rate of the temperature increase (v_m) of *meta* and *para* isomers gave analogous diagrams.

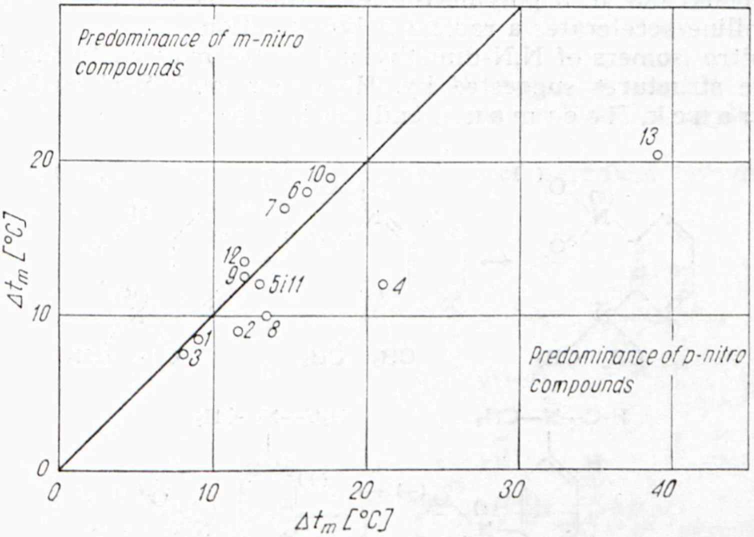


Fig. 11. Comparison of influence of *meta* nitro compounds against *para* nitro compounds on drop of peak exotherm temperature (Δt_m) of standard polyester resin: *1* — nitrotoluene, *2* — diphenyl, *3* — benzyl alcohol, *4* — benzaldehyde, *5* — benzoic acid, *6* — chloronitrobenzene, *7* — bromonitrobenzene, *8* — nitrophenol, *9* — nitroanisole, *10* — nitro-N,N-dimethylaniline, *11* — nitroacetanilide, *12* — nitro-N-methylacetanilide, and *13* — dinitrobenzene

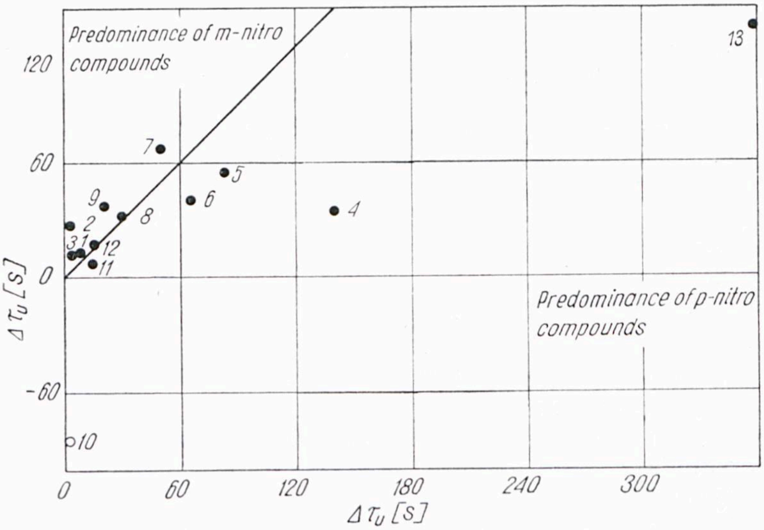
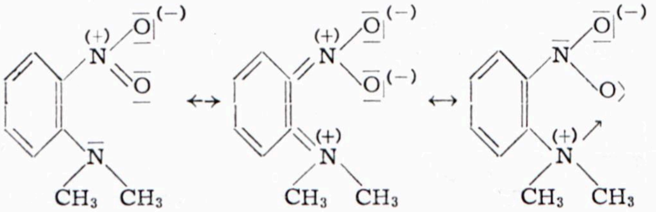
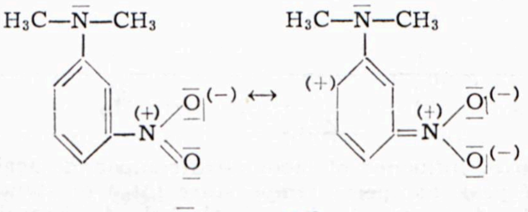


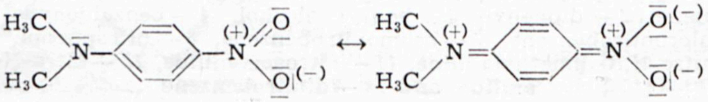
Fig. 12. Comparison of influence of *meta* nitro compounds against *para* nitro compounds on the increase of cure time ($\Delta\tau_u$) of standard polyester resin: *1* — nitrotoluene, *2* — diphenyl, *3* — benzyl alcohol, *4* — benzalaldehyde, *5* — benzoic acid, *6* — chloronitrobenzene, *7* — bromonitrobenzene, *8* — nitrophenol, *9* — nitroanisole, *10* — nitro-N,N-dimethylaniline, *11* — nitroacetanilide, *12* — nitro-N-methylacetanilide, and *13* — dinitrobenzene

To elucidate the influence of the position of nitro group in the ring on radical polymerization, we considered the electronic structure of nitro isomers of N,N-dimethylaniline. These isomers show the most differences in their behaviour in a polymerizable medium. Besides, *m*-nitro-N,N-dimethylaniline accelerates a radical polymerization.

For nitro isomers of N,N-dimethylaniline we may write the following resonance structures suggested by Horner and Scherf[6], as well as by Franck, Hoermann, and Scheibe[7]:







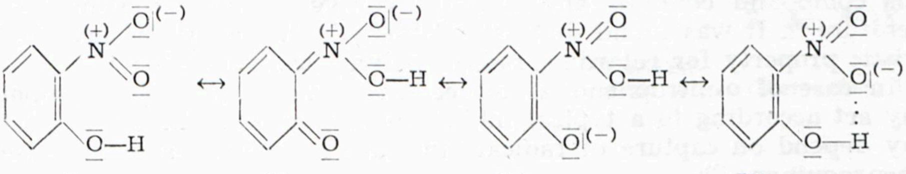
As is shown above an amino group remains unchanged only in *m*-nitro-N,N-dimethylaniline and it does not take part in mesomeric structures.

Accordingly, the action of mentioned nitro compound can be elucidated by way of independent action of both groups — nitro group as retarding and an amino group as accelerating radical polymerization.

Since the action of the amino group is stronger than that of the nitro group *m*-nitro-N,N-dimethylaniline accelerates radical polymerization. In the other isomers the influence of amino group is reduced because of its part in mesomeric structures and, therefore, the influence of nitro group is comparatively vigorous. We suppose that the abnormal action of all nitro isomers of N,N-dimethylaniline is caused in the first place by the presence of peroxide initiator, because it is generally understood that tertiary amines activate these initiators.

The appreciable differences in the retarding action of radical polymerization by nitro isomers of benzaldehyde and of dinitrobenzene can be explained by analogous method as in the case of nitro isomers of N,N-dimethylaniline, i.e. by considering their mesomeric structures.

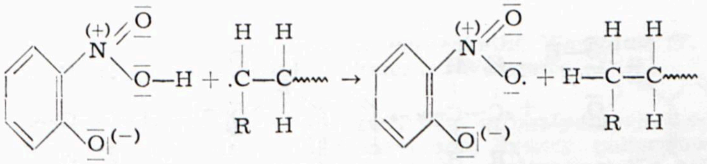
Afterwards we focussed our attention on the superactivity of o-nitrophenol and of o-nitroacetanilide in retarding action of radical polymerization. It is necessary to expect that the action of these compounds can run in a different way from nitrobenzene, as it was presented in our previous paper [1]. It may be expected that the mesomeric structures for o-nitrophenol will be as follows:



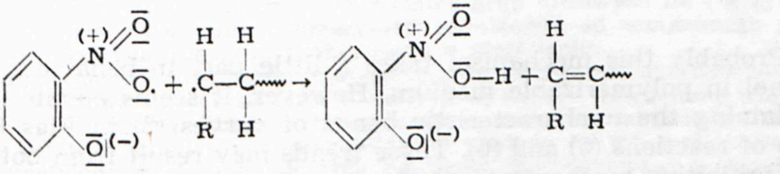
I II III IV

In structure IV an internal hydrogen bond should be considered as was shown in the various papers [8-10]. The same problem is applicable for o-nitroacetanilide [11-13].

We suppose that the expected retarding of a radical polymerization by o-nitrophenol is as follows:

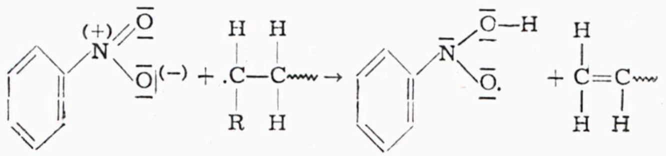


(1)



(2)

The reactions (1) and (2) are to be more effective than it was given in the case of reactions for nitrobenzene in our previous paper [1]:



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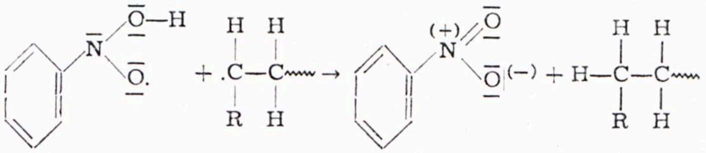


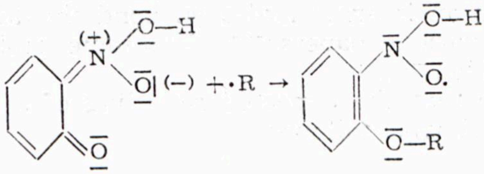
(4)

In reactions (3) and (4) the nitro compound mediates in the transfer of hydrogen atom only, while in reactions (1) and (2) a hydrogen atom, which participates in the retarding action of radical polymerization, belongs to *o*-nitrophenol. We suppose, therefore, that reaction (2) is much more effective than reaction (3).

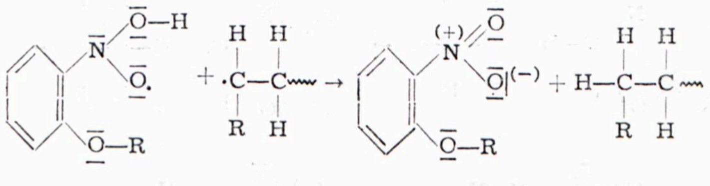
The mentioned reasons are confirmed by "normal" behavior of *o*-nitroanisole and *o*-nitro-N-methylacetanilide in polymerizable medium as it was shown in Figs 4 and 6 as well as in Table 1. In these compounds non-active methyl group is presented instead of active hydrogen atom.

Because of presence of the internal hydrogen bond in the mentioned nitro compounds an experiment with salicylaldehyde was carried out. This compound contains an internal hydrogen bond according to the literature [14]. It was found that salicylaldehyde did not show any characteristic property for retarding radical polymerization (Table 1).

In case of *o*-nitrophenol it is necessary to add that this compound may act according to a typical inhibition mechanism. Thus, the reaction may depend on capture of radical "in statu nascendi" as in the case of *p*-benzoquinone [15]:



(5)



(6)

Probably this mechanism takes a little part in behaviour of *o*-nitrophenol in polymerizable medium. However, it seems possible to attempt explaining the uncharacteristic bends of curves (2) in Figs 8 and 9 by help of reactions (5) and (6). These trends may result from both retarding and inhibiting mechanism, which were proposed in reactions (1) and (2), as well as (5) and (6). The same argumentation should be analogous in the case of *o*-nitroacetanilide.

To summarize, we can conclude, that the differences in behaviour of particular nitro compounds in polymerizable medium can be explained by means of the hypothesis, which was given in our previous paper 1). According to us various activities of nitro compounds in mediating the transfer of hydrogen atom between polymerizing macroradicals are the main cause of the differences in retarding action of radical polymerization.

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REFERENCES

1. Buźniak J., Urbański T., *Polimery,* **15**, 333 (1970).
2. Hartel H., *Chimia,* **19**, 116 (1965).
3. Mondvai I., Gal J., *Magy. Kem. Folyoirat,* **72**, 473 (1966).
4. Mondvai I., Halasz L., Keschitz A., *Magy. Kem. Folyoirat,* **75**, 353 (1969).
5. Hammond G. S., Bartlett P. D., *J. Polymer Sci.,* **6**, 617 (1951).
6. Horner L., Scherf K., *Ann.,* **574**, 202 (1951).
7. Franck B., Hoermann H., Scheibe S., *Chem. Ber.,* **90**, 330 (1957).
8. Urbański T., Dąbrowska U., *Bull. Acad. Polon. Sci., ser. chim. geol. et geogr.,* **7**, 235 (1959).
9. Dąbrowska U., Urbański T., *Roczniki Chem.,* **37**, 805 (1963).
10. Dąbrowska U., Urbański T., Witanowski M., Stefaniak L., *Roczniki Chem.,* **38**, 1323 (1964).
11. Chaplin H. O., Hunter L., *J. Chem. Soc.,* **1938**, 375.
12. Луцкий А. Е., Кондратенко Б. П., *ЖОХ,* **29**, 2073 (1959).
13. Луцкий А. Е., Конельская Б. Н., Кондратенко Б. П., *ЖОХ,* **30**, 3782 (1960).
14. Morton R. A., Stubbs A. L., *J. Chem. Soc.,* **1940**, 1347.
15. Bevington J. C., Ghanem N. A., Melville H. W., *J. Chem. Soc.,* **1955**, 2822.

WPŁYW AROMATYCZNYCH ZWIĄZKÓW NITROWYCH NA OPÓŹNIANIE POLIMERYZACJI RODNIKOWEJ. II. WPŁYW DWUPODSTAWIONYCH POCHODNYCH BENZENU

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Zbadano wpływ kilkudziesięciu nitrozwiązków aromatycznych dwupochodnych benzenu na przebieg kopolimeryzacji nienasyconej żywicy poliestrowej „Polimal 109” jako żywicy wzorcowej. Badane nitrozwiązki porównywano z nitrobenzenem, używając je w stężeniu $2 \cdot 10^{-5}$ gramorównoważnika grup nitrowych na 1 g żywicy. Stwierdzono zależność opóźniania polimeryzacji rodnikowej od wzajemnego położenia grupy nitrowej i innych grup funkcyjnych w pierścieniu.

W przypadku mononitrozwiązków stwierdzono, że szczególnie aktywne okazały się pochodne *orto*, a wśród nich związki, w których występuje wewnętrzne wiązanie wodorowe z grupą nitrową. Zbadano szczegółowo w szerokim zakresie stężeń zachowanie się *o*-nitrofenolu i *o*-nitroacetanilidu ze względu na ich wyjątkową aktywność i uzupełniono w stosunku do tych związków zaproponowany poprzednio 1) nowy mechanizm oddziaływania nitrozwiązków aromatycznych z polimeryzującymi łańcuchami. Stwierdzono, że *m*-nitro-N,N-dwumetyloanilina, jako jedyny badany nitrozwiązek aromatyczny, działał przyśpieszająco na polimeryzację rodnikową. Mogło

to być spowodowane aktywacyjnym wpływem III-rzędowej aminy na inicjator nadtlenkowy. Przypuszczalnie wpływowi temu należy również przypisać pewną niestałość parametrów $\tau_{\dot{z}}$ i τ_{u}, zależną od okresu indukcji żywicy wzorcowej.

W przypadku dwóch grup nitrowych w pierścieniu związkiem najbardziej aktywnym okazał się *p*-dwunitrobenzen.