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Volatility of Some Aromatic Nitrosubstituted Plasticizers for Polymers

A. E. Golubev[a]*, I. V. Novikov[b], S. A. Kuvshinova[b],**
V. A. Burmistrov[b]*, and O. I. Koifman[b,c]******

[a] *Research Institute of Polymer Materials, ul. Chistopol'skaya 16, Perm, 614101 Russia*
*e-mail: *niipm@perm.ru; **sofya.kuv@yandex.ru; ***burmistrov@isuct.ru; ****oik@isuct.ru*
[b] *Ivanovo State University of Chemistry and Technology, Sheremetevskii pr. 7, Ivanovo, 153000 Russia*
[c] *Krestov Institute of Solution Chemistry, Russian Academy of Sciences,*
ul. Akademicheskaya 1, Ivanovo, 153045 Russia

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Abstract—Nine derivatives of nitrophthalic acids and nitrophenols were synthesized as potential plasticizers for polymers and structurally characterized by ^{1}H NMR and elemental analysis. The time dependences of the weight loss for the nitro derivatives synthesized and for commercial plasticizers (dibutyl phthalate and dioctyl phthalate) were obtained by gravimetric method at 100ºC, and their volatilities and dipole moments were calculated. The resultant nitroplasticizers are considerably less volatile than dibutyl phthalate. Low volatility is associated not so much with high molecular weight as with high polarity. The nitroplasticizers are well compatible with cellulose esters and exhibit low rates of migration from polymer films.

Keywords: volatility, nitrosubstituted plasticizers, dibutyl phthalate, cellulose esters, dipole moments, polarity, polymer

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INTRODUCTION

Hard-chain polymers, e.g., polyvinylchloride, cellulose diacetate, nitrocellulose, etc., exhibit increased brittleness, which renders practically impossible the use of products thereof under low temperature conditions. The low-temperature properties of polymers and products thereof can be improved, and their processing temperature can be reduced, through the use of plasticizers, special agents increasing the mobility of the structural elements of polymers [1–4]. This increases the deformability of the plasticized polymer, broadens the range of their service temperatures toward lower temperatures, reduces the brittleness temperature, and improves the processabilty of polymers in melt [3, 4].

Currently, there exists a fairly wide range of commercial plasticizers [2, 5, 6], among which esters of phthalic acid and aliphatic alcohols (phthalates) are recognized as the major group [7, 8]. Being inexpensive, phthalates exhibit high heat resistance, good plasticizing efficiency, and high photostability and are compatible with many polymers. Even when introduced in relatively small amounts into polymers, low-molecular-weight derivatives of phthalic acid solvate the polar groups of the latter, thereby weakening their interactions [9]. In [10], this process was effectively promoted via introduction of polar moieties, e.g., nitro groups, into the structure of potential plasticizers. High polarity of dialkoxyethyl-4-nitrophthalates was shown [10] to enhance their thermodynamic affinity to nitrocellulose, thereby eventually improving the compatibility and effectiveness of the plasticizing action.

Further properties of chemical additives that make them suitable as plasticizers are high boiling point (>250°C) and flash point (>160°C), low flammability, chemical resistance to various agents (fuels, oils, etc.), thermal and photochemical stability, non-toxicity, and inexpensiveness [11]. Virtually the main recognized characteristic of potential plasticizers is low volatility at the polymer processing and service temperatures.

Specifically high volatility of dibutyl phthalate (DBP), despite all the advantages, poses certain constraints on its use as plasticizer. However, data on the volatility of the substances making part of polymer compositions are scarce and, moreover, scattered and often random. For example, volatilities of new plasticizers for polyvinylchloride, interaction products of fatty acids and 1,4-butanediol, were reported in [12]. The volatility of phenolic and amine stabilizers of polymers was estimated in [13].

In view of the above-said, we estimated herein the volatility of a number of potential plasticizers of polymer compositions, derivatives of nitrophthalic acids and nitrophenols, and determined how this characteristic is affected by the chemical structure of the compounds tested.

EXPERIMENTAL

In our experiments, 3- and 4-nitrophthalic acids, 2,4-dinitrophenol, *n*-butyl, *n*-propyl, and ethyl alcohols, propionyl chloride, amyl bromide, bromohexadecane, potash, dimethylformamide, triethylamine, and chloroform (all purchased from Sigma-Aldrich) were used without further purification. 4-Nitrophenol ("Vekton") was recrystallized from water, and 2,5-dinitrophenol ("Vekton"), from a 2 : 3 ethanol-water mixture. Plasticizers dioctyl phthalate (DOP) and DBP (OOO Roshal' Plasticizers Plant, Moscow oblast) were used without further purification.

The ^{1}H NMR spectra were recorded, and the chemical shifts were measured on a Bruker-Avance **3** high-resolution spectrometer (operating frequency 500 MHz); $CDCl_3$ was used for proton stabilization. Chemical shifts were measured relative to tetramethylsilane in ppm (δ-scale) accurately to within 0.01 ppm.

Elemental analysis data were obtained with a Flash EA 1112 Series CHNS-O Analyzer.

The volatility of the commercial and synthesized plasticizers was determined from the loss in weight of the substance over time in the setup shown schematically Fig. 1.

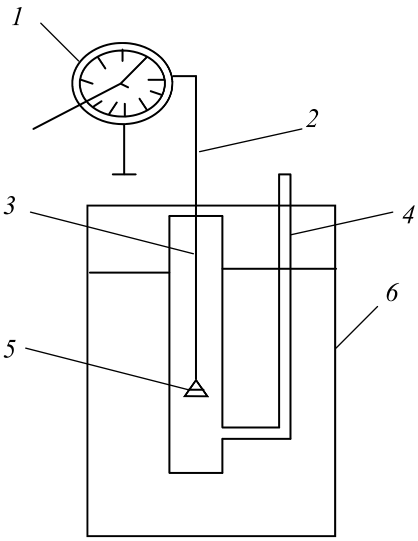


Fig. 1. Schematic diagram of the setup for volatility determination: (*1*) torsion balance (weighing range 500 mg, division value 1 mg), (*2*) metallic thread, 0.05 mm in diameter, (*3*) glass tube, 30 mm in diameter, (*4*) branch for gas supply, (*5*) glass cup, 14.5 mm in diameter and 5 mm in height, for the weighed portion of the plasticizer, and (*6*) thermostat.

A glass cup with the weighed portion of the plasticizer was suspended by a metallic thread to the lever of the torsion balance. The thermostat temperature was adjusted with a contact thermometer accurately to within 0.5°C. The correspondence between the temperatures of the coolant in the thermostat and of the gas inside the tube at the sample level was checked by using control mercury thermometers. The thermostat was preheated to the preset temperature, and the weighing operation was performed immediately after the cup with the weighed portion of the sample sank. As a result of the measurements, the time dependence of the weight loss was plotted.

Di-*n*-butyl ester of 4-nitrophthalic acid (1). 0.1 mol of 4-nitrophthalic acid, 0.5 mol of butanol-1, and a catalytic amount (1.5% of the weight of 4-nitrophthalic acid) of concentrated sulfuric acid were placed in a round-bottomed flask equipped with a Dean-Stark trap, a reflux condenser, and a stirrer. The reaction mixture was heated with stirring to boiling of the reaction mixture and separation of a part of the alcohol and the reaction water in the trap. Upon heating for 15 h the excess alcohol was distilled off. To remove acidic impurities (residues of sulfuric acid, alkyl sulfuric acid, 4-nitrophthalic acid, and monoalkyl phthalate) the product was poured into water and alkalified with 20% soda solution to a slightly alkaline reaction. Next, the product was extracted with chloroform, the organic layer was washed several times with water in a separatory funnel, separated, dried with anhydrous sodium sulfate, and filtered. Silica gel was poured into the product solution in chloroform, left for 1 h, and filtered. Chloroform was distilled off. Yield

96%, light yellow oily liquid. Found, %: C 59.03; H 6.37; N 4.17. $C_{16}H_{21}NO_6$. Calculated, %: C 59.43; H 6.55; N 4.33. ^{1}H NMR spectrum, δ, ppm: 8.38 s; 8.20 d; 7.68 d (3H, Ar); 4.19 t (4H, OCH_2); 1.59 m (4H, CH_2); 1.30 m (4H, CH_2); 0.81 t (6H, CH_3).

Di-*n*-propyl and diethyl esters of 4-nitrophthalic acid, as well as di-*n*-butyl and di-*n*-propyl esters of 3-nitrophthalic acid, were obtained under similar conditions at the same ratio of reactants.

Di-*n*-propyl ester of 4-nitrophthalic acid (2). Yield 97%, light yellow oily liquid. Found, %: C 56.57; H 5.63; N 4.53. $C_{14}H_{17}NO_6$. Calculated, %: C 59.43; H 6.55; N 4.33. ^{1}H NMR spectrum, δ, ppm: 8.55 s; 8.33 d; 7.82 d (3H, Ar); 4.27 t (4H, OCH_2); 1.75 m (4H, CH_2); 0.96 t (6H, CH_3).

Diethyl ester of 4-nitrophthalic acid (3). Yield 97%, light yellow solid, mp 25°C. Found, %: C 53.60; H 4.78; N 5.16. $C_{12}H_{13}NO_6$. Calculated, %: C 53.93; H 4.90; N 5.24. ^{1}H NMR spectrum, δ, ppm: 8.51 s; 8.30 d; 7.77 d (3H, Ar); 4.34 m (4H, OCH_2); 1.34 t (6H, CH_3).

Di-*n*-butyl ester of 3-nitrophthalic acid (4). Yield 95%, colorless oily liquid. Found, %: C 59.31; H 6.42; N 4.09. $C_{16}H_{21}NO_6$. Calculated, %: C 59.43; H 6.55; N 4.33. ^{1}H NMR spectrum, δ, ppm: 8. 00 t (1H, Ar); 7.97 t (1H, Ar); 7.26 t (1H, Ar); 4.25 t (3H, OCH_2); 4.21 t (3H, OCH_2); 1.55 m (8H, CH_2); 0.91 t (6H, CH_3).

Di-*n*-propyl ester of 3-nitrophthalic acid (5). Yield 96%, colorless oily liquid. Found, %: C 56.77; H 5.69; N 4.60. $C_{14}H_{17}NO_6$. Calculated, %: C 59.43; H 6.55; N 4.33. ^{1}H NMR spectrum, δ, ppm: 8.28 d (1H, Ar); 7.68 m (2H, Ar); 4.36 t (2H, OCH_2); 4.28 t (2H, OCH_2); 1.77 m (4H, CH_2); 0.99 t (6H, CH_3).

2,4-Dinitrophenyl ester of propionic acid (7). Into a three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel, 0.1 mol of 2,4-dinitrophenol, 70 mL of chloroform, and 15 mL of triethylamine were placed. Into the solution thus obtained, 0.1 mol of propionic acid chloride was added dropwise with vigorous stirring for 30 min. The resulting mixture was stirred for 2 h at room temperature and then refluxed for 12 h. Next the solvent was distilled off, whereupon the residue was transferred into ice-cold water and left for 2 h. The product was filtered off, washed with water, and dried. For purification the product was recrystallized from ethanol and subjected to column chromatography over silica gel (eluent chloroform). Yield 92%, yellow platelet crystals, mp 72°C. Found, %: C 44.85; H 3.22; N 11.54. $C_9H_8N_2O_6$. Calculated, %: C 45.01; H 3.36; N 11.66.

2,5-Dinitrophenyl ester of propionic acid (6) was prepared by a procedure similar to that used for ester **7**. Yield 88%, yellow platelet crystals, mp 84°C. Found, %: C 44.87; H 3.21; N 11.53. $C_9H_8N_2O_6$. Calculated, %: C, 45.01; H 3.36; N 11.66.

Pentyloxy-2,5-dinitrobenzene (9). The reaction mixture consisting of 0.11 mol of 2,5-dinitrophenol, 0.5 mol of potash, and 0.1 mol of amyl bromide in 150 mL of dimethylformamide was refluxed under vigorous stirring for 10 h, then cooled, poured into ice-cold water, and left for 3–5 h. The product was extracted with ether, the organic layer was washed 5–7 times with water, separated in the separatory funnel, and dried with anhydrous sodium sulfate, whereupon the solvent was distilled off. For purification, the product was recrystallized from ethanol and subjected to column chromatography over silica gel (eluent chloroform). Yield 87%, reddish yellow shiny crystals, mp 36°C. Found, %: C 51.90; H 5.48; N 10.96. $C_{11}H_{14}N_2O_5$. Calculated, %: C 51.97; H 5.55; N 11.02. ^{1}H NMR spectrum, δ, ppm: 7.90 m (3H, Ar); 4.21 t (2H, OCH_2); 1.88 m (2H, CH_2); 1.47 m (2H, CH_2); 1.40 m (2H, CH_2); 0.93 t (3H, CH_3).

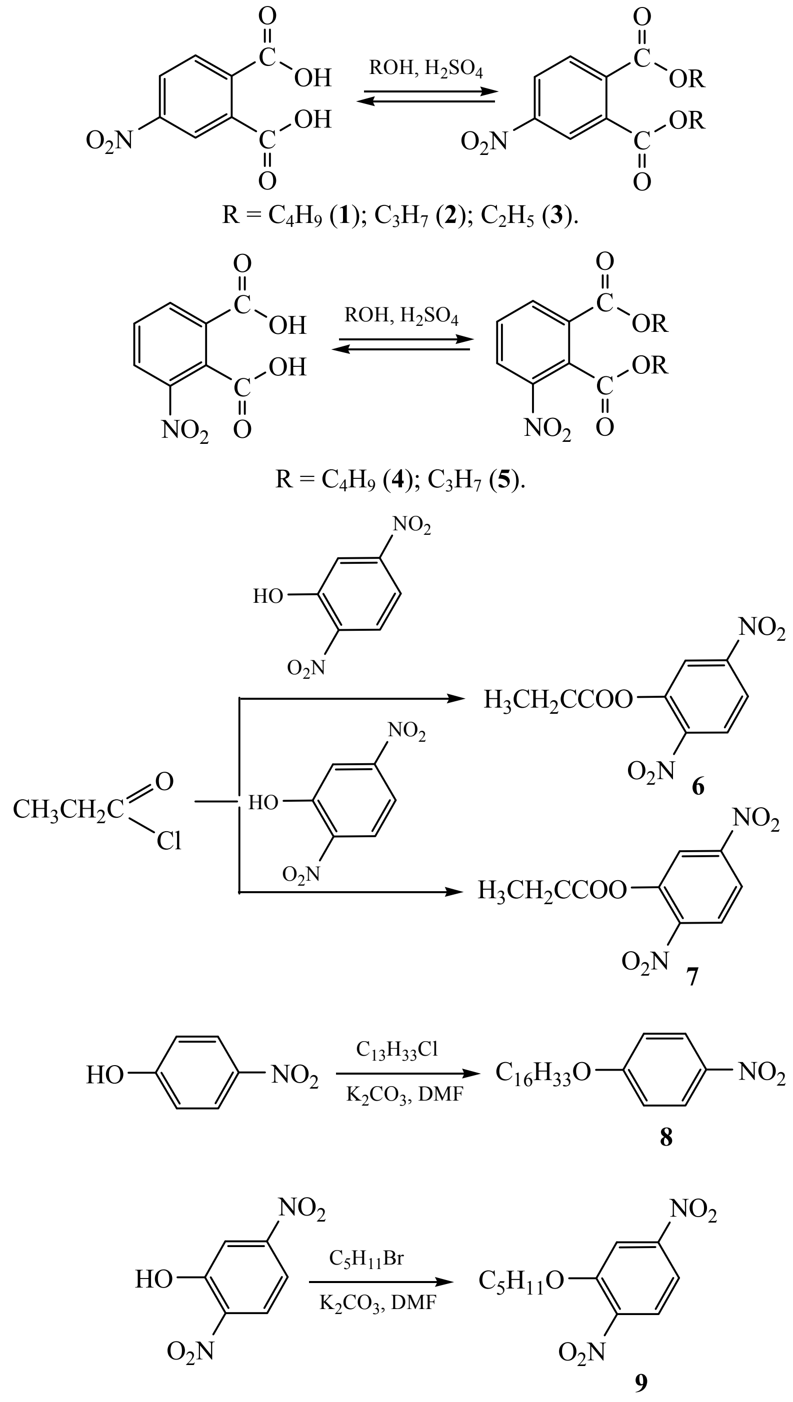
Hexadecanoxy-4-nitrobenzene (8) was prepared under conditions and reactant ratios identical to those used for **9**. Yield 73%, light yellow crystals, mp 62°C. Found, %: C 72.60; H 10.19; N 3.78. $C_{22}H_{37}NO_3$. Calculated: C 72.69; H 10.26; N 3.85. ^{1}H NMR spectrum, δ, ppm: 8.21 d (2H, NO_2-Ar); 6.96 d (2H, Ar-OCH_2); 4.06 t (2H, OCH_2); 1.83 m (2H, CH_2); 1.48 m (2H, CH_2); 1.27 m (24H, CH_2); 0.89 t (3H, CH_3).

RESULTS AND DISCUSSION

Di-*n*-butyl, di-*n*-propyl, and diethyl esters of 4-nitrophthalic acid (**1, 2,** and **3**, respectively), di-*n*-butyl and di-*n*-propyl esters of 3-nitrophthalic acid (**4** and **5**), 2,5- and 2,4-dinitrophenyl esters of propionic acid (**6** and **7**, respectively), hexadecanoxy-4-nitrobenzene (**8**), and pentyloxy-2,5-dinitrobenzene (**9**) (see Scheme 1) were synthesized as research subjects, potential plasticizers.

Nitrophthalates **1–5** were prepared by esterification of 4- or 3-nitrophthalic acids with appropriate alcohols in the presence of catalytic amounts of concentrated sulfuric acid. To this end, the reaction mixture was refluxed for 8–12 h using a 5-fold excess of alcohol.

Scheme 1.



R = C_4H_9 (**1**); C_3H_7 (**2**); C_2H_5 (**3**).

R = C_4H_9 (**4**); C_3H_7 (**5**).

6

7

8

9

Prolonged heating is required for the esterification of 3-nitrophthalic acid due to steric limitations in the synthesis of di-*n*-butyl phthalates as well.

Dinitrophenols were acylated with propionic acid chloride by refluxing equimolar amounts of the reactants in chloroform in the presence of triethylamine as hydrogen chloride acceptor (esters **6** and **7**). Nitrophenols were alkylated with haloalkyls in dimethylformamide in the presence of potash (compounds **8** and **9**).

The structure of the compounds synthesized was confirmed by elemental analysis and ^{1}H NMR spectro-

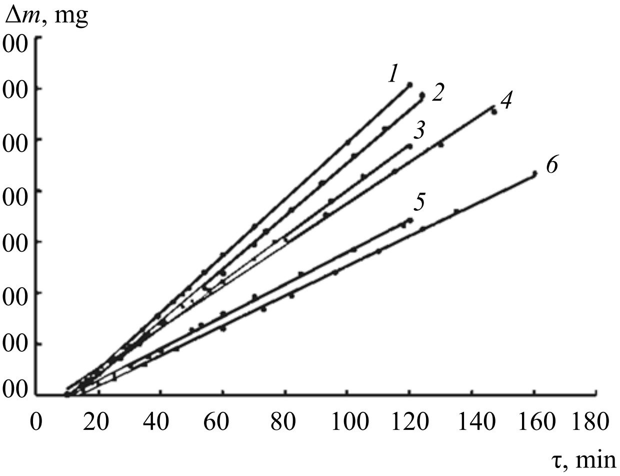


Fig. 2. Time dependences of the weight loss for phthalates: (*1*) DBP, (*2*) **1**, (*3*) **2**, (*4*) **5**, (*5*) **4**, and (*6*) **3**.

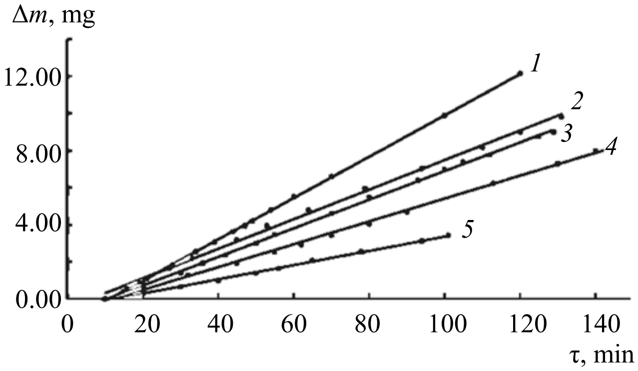


Fig. 3. Time dependences of the weight loss for nitrophenol derivatives: (*1*) DBP, (*2*) **6**, (*3*) **7**, (*4*) **9**, and (*5*) **8**.

scopy. For the elemental analysis data and for the yields and melting points of the end products, as well as for the assignment of the signals in the spectra, see Experimental.

Most polymers are processed in melt at elevated temperatures, which makes volatility (evaporation rate) one of the main characteristics of plasticizers. The volatility of plasticizing additives is essential in evaluating their effectiveness. For example, during heat treatment of polymer compositions or during service of products thereof, some part of plasticizers can migrate from the polymer without being involved in the plasticization, thereby deteriorating the consumer qualities of films, fibers, membranes, etc. In this connection, we studied the volatility of the potential plasticizers synthesized by the gravimetric method at 100°C. The choice of this temperature was dictated by the fact that nitrocellulose etrols (celluloid) are processed at temperatures above their softening point of 80–90°C. For comparison, under identical conditions we determined the volatility of DBP and DOP as the most widely used plasticizers.

The time dependences of the weight loss (Figs. 2 and 3) for all the compounds tested are approximated by straight lines due to a constant evaporation rate observed at unchanged temperature and evaporation

Table 1. Volatility and dipole moments of the plasticizers

Plasticizer	Molecular weight *M*, g/mol	Weight loss after 1 h, g/h	Volatility, mg cm^{-2} h^{-1}	Volatility relative to DBP	Dipole moment *D*, D (AM1)
DOP	390.56	4.15	3.24	0.81	2.2
DBP	278.40	6.60	3.98	1.00	2.7
1	323.34	5.90	3.63	0.91	5.5
2	295.29	5.10	3.24	0.81	5.7
3	267.24	3.35	2.00	0.50	5.2
4	323.34	3.85	2.26	0.57	6.1
5	295.29	5.30	3.08	0.77	6.3
6	240.17	5.33	3.11	0.78	1.8
7	240.17	4.61	2.77	0.70	4.9
8	363.54	2.10	1.35	0.34	6.7
9	254.24	3.45	2.15	0.54	2.4

Table 2. Volatility of the film samples

Polymer	Plasticizer	Weight loss after 1 h, mg/h	Volatility, mg cm^{-2} h^{-1}
CDA	DBP	0.0042	0.95
CDA	**1**	0.0035	0.76
CDA	**9**	0.0017	0.40
NC	DBP	0.0025	0.56
NC	**1**	0.0018	0.46

area. The same induction period for all samples (~10 min) was observed due to arising of nonstationary evaporation during heating of the plasticizers to the experimental temperature. We associate the occurrence of an induction period with heat transfer exclusively, and this is confirmed by its independence on the nature of the compounds studied.

Table 1 lists the experimental volatilities of the plasticizers and their dipole moments calculated by the AM1 method. These data do not reveal unambiguous trends in the influence exerted on these characteristics by the molecular structure of the compounds of interest. Obviously, the volatility of a substance is directly related to its cohesion energy which, in turn, is determined by various contributions, from both Van der Waals forces and specific forces, to the intermolecular interaction energy. The intensity of the dispersion interactions is mainly determined by the size and polarizability of the molecules, while the dipole-dipole contacts are directly associated with the molecular dipole moments. Moreover, each of the interaction types is directly affected by the molecular geometry: symmetry, complementarity, and conformational transition capability. Hence, a lower volatility of DOP as compared to DBP is attributable to a substantially larger weight of the molecule of the former and to enhanced dispersion interactions. In the case of compounds **1, 2, 4, 5,** and **8**, the volatility may be suppressed upon introduction of a nitro group into the molecule because of increases in both the weight and polarity.

Notably, progressive lengthening of aliphatic substituents caused the volatility of the 4-nitrophthalate diesters to markedly increase as **3** < **2** < **1** (Table 1, Fig. 2, curves *1*–*3* and *6*). This experimental fact cannot be explained by the effect of the dipole moment exclusively. In our opinion, it can be reasonably interpreted as due to enhancement of the loosening effect of alkyl substituents with their lengthening, which weakens the dipole-dipole interactions, thereby decreasing the cohesion energy. This assumption is indirectly confirmed by the fact that 4-nitrophthalic acid diethyl ester **3**, despite its smallest size among the nitrophthalates, is a solid at room temperature. As known, the crystal lattice energy is maximal at the closest rapprochement of interacting molecules, which is least hindered by short substituents in diester **3**. Most likely, the same factors are responsible for low volatility of dinitrophenol derivatives **6, 7,** and **9**, which have the lowest molecular weights and dipole moments among the substances of interest, but which are crystalline products.

Considering significantly lower volatilities of the alkoxynitrophthalates and substituted nitrophenols synthesized as compared to DBP it was reasonable to expect their higher thermodynamic affinity with polymers and, consequently, lower migration rates from polymers at high temperatures. To check the assumption, we plotted the time dependences of the

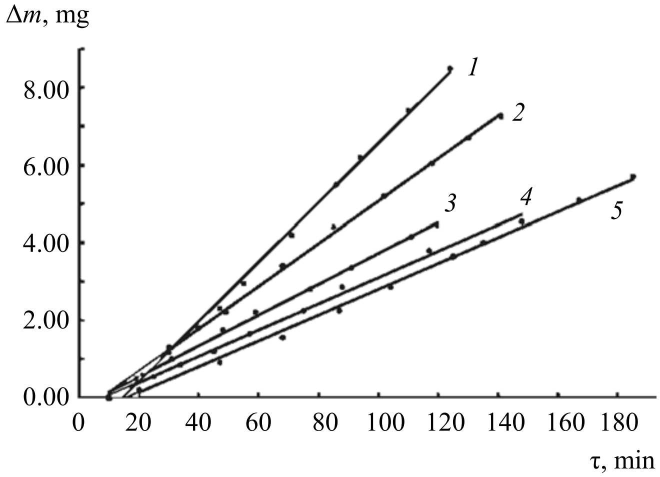


Fig. 4. Time dependences of the weight loss of the CDA- and NC-based film samples: (*1*) CDA + DBP, (*2*) CDA + **1**, (*3*) NC + DBP, (*4*) NC + **1**, (*5*) CDA + **9**.

weight loss of the film samples based on cellulose diacetate (CDA) and cellulose nitrate (NC, nitrogen content 11%) (Fig. 4). The films were prepared by dry spinning from 10% solutions in cyclohexanone. As plasticizers for testing we chose di-*n*-butyl ester of 4-nitrophthalic acid (**1**) as a structural analog of DBP and pentyloxy-2,5-dinitrobenzene (**9**) as the least volatile among the substances synthesized. The results were compared with those for the films plasticized with DBP. The content of the plasticizers in all the samples was identical, 23 wt%. Prior to the experiment the films were dried with subsequent evacuation at a residual pressure of 200 Pa at 313.15±1 K to constant weight. The film thickness measured with an ISV-1 thickness gauge accurately to within 0.5 μm was 37–41 μm.

Like with individual compounds, the time dependences of the weight loss of the film samples are represented by straight lines and exhibit an induction period identical for all the films as associated with the heat transfer during heating to the experimental temperature (Fig. 4). Table 2 provides insights into the rate of migration of the plasticizers from the polymers during service at elevated temperatures. It is seen that both the CDA- and NC-based films, plasticized with nitrosubstituted dibutyl phthalate **1** and dinitro derivative **9**, are less volatile than the films plasticized with DBP. In our opinion, this is due to the ability of the nitroplasticizers to interact effectively with polymer macromolecules via solvating their polar groups and to stay longer in the polymer, thereby preserving its elastic properties.

CONCLUSIONS

Thus, nine new derivatives of nitrophthalic acids and nitrophenols were synthesized and structurally identified. Time dependences of the weight loss of the potential plasticizers were obtained by gravimetric method at 100°C, and their volatilities and dipole moments were calculated. By contrast to DBP, all the substances synthesized were characterized by high polarity and low volatility. This allows them to be well-compatible with polymers, in particular with cellulose nitrates and acetates, and to be able to effectively reduce their glass transition temperature and to decrease the migration rate from polymer films, thereby preserving their good physicomechanical properties.

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