Technical Physics Letters, 2023, Vol. 49, No. 2

06.4;15.2

Investigation of some low-temperature characteristics of plasticizers based on ethylene glycol

© *S.M. Putis, A.Yu. Mershin, S.A. Dushenok*

FSUE „SCTB „Technolog“, Russia, St. Petersburg
E-mail: sergey_mi79@mail.ru

Received July 27, 2022
Revised November 19, 2022
Accepted November 21, 2022

The results obtained by studying the low-temperature characteristics of diols (ethylene glycol and its derivatives) and their nitroesters by the differential scanning calorimetry method are presented. It is shown that the studied compounds are characterized by glass transition temperatures in the range from −73 to −103°C, while ethylene glycol and its dinitrate differ from other compounds in the presence of crystallization and melting temperatures under experimental conditions.

Keywords: Differential scanning calorimetry, ethylene glycol and its derivatives, glass transition temperature.

DOI: 10.21883/TPL.2023.02.55359.19323

Various plasticizers are introduced into polymer materials tailored to specific applications in order to adjust their parameters (hardness, brittleness, thermal stability, etc.) as needed. Notably, the molecular mass (MM) of a typical plasticizer is much lower than the one of polymers [1,2]. The plasticizer content in the final product with the required characteristics may vary from 5 to 90% [3]. Plasticizers are used in different industry fields. An example here is provided by energetic plasticizers that are used in composite solid propellants consisting of an oxidizer, fuel, and a polymer binder [4]. Derivatives of di- and polyatomic alcohols (diols, triols, etc.) [2], such as nitrates (nitroglycerin, diethylene glycol dinitrate, triethylene glycol dinitrate, or their mixtures) [5], and azide and azido-ester plasticizers [4,6] belong to this class of plasticizers. andThe key requirements imposed on plasticizers include fine chemical compatibility with polymers and other components of mixtures, low volatility and toxicity, etc. [7]. Glass transition temperature T_g is one of the most important characteristics of binders (mixtures of polymers with plasticizers). In most cases, T_g of a binder does not depend on the parameters of a polymer and is specified by the plasticizer polarity. Depending on the plasticizer polarity, T_g of mixtures may be governed by either Fox and Couchman–Karasz equations or the Jenkel–Heusch equation [8]. The main parameter of these equations is T_g of individual polymer and plasticizer substances. While T_g is a characteristic feature of polymers, T_g of plasticizers has almost never been determined [1,2], and no data on T_g of energetic plasticizers are available [3–6,9].

In the present study, we examine the low-temperature characteristics of certain liquid plasticizers based on ethylene glycol by differential scanning calorimetry (DSC) performed using the Netzsch DSC214 „Polyma“ as instrument. The compounds chosen for study were ethylene glycol (EG, sample No. 1), its derivatives (diethylene glycol (DEG, sample No. 3), triethylene glycol (TEG, sample No. 5), 1,2-propylene glycol (1,2-PG, sample No. 7), ethylene-propylene glycol (EPG, sample No. 9), and dipropylene glycol (DPG, sample No. 11)), and products of their nitration (dinitrates): ethylene glycol dinitrate (EGDN, sample No. 2), diethylene glycol dinitrate (DEGDN, sample No. 4), triethylene glycol dinitrate (TEGDN, sample No. 6), 1,2-propylene glycol dinitrate (1,2-PGDN, sample No. 8), ethylene-propylene glycol dinitrate (EPGDN, sample No. 10), and dipropylene glycol dinitrate (DPGDN, sample No. 12). The structure and purity of plasticizers was verified by NMR spectroscopy and gas-liquid chromatography, and the lack of traces of moisture was established by the Karl Fischer method. Low-temperature characteristics were determined in accordance with the procedure outlined in [10] within the temperature range from 25 to −140°C at a scan rate of 10°C/min (in cooling and heating modes). It was demonstrated that the studied plasticizers (with the exception of samples Nos. 1 and 2) do not crystallize when cooled; instead, they undergo a transition from a state of viscous flow to a glass state at a certain characteristic transition temperature. The reverse transition from a glass state to a state of viscous flow in the process of heating of a supercooled sample is characterized by T_g. The results of examination of the chosen plasticizers are listed in the table.

It can be seen from the table that the indicated diols and their dinitrates are compounds with different MM values (from ∼ 62 to ∼ 240 g/mol) and fairly low glass transition temperatures. Samples Nos. 1 and 2 are an exception here: they enter a solid crystalline state when cooled and are characterized by crystallization (under cooling) and melting (under heating) temperatures in the conditions of our experiments (Fig. 1).

The process of crystallization of supercooled samples Nos. 1 and 2 is marked by intense exothermic effects (Fig. 1, *a*). Crystallization enthalpy ΔH_{cr} of these samples is 136.7 and 86 J/g, respectively. An endothermic effect

Molecular mass, transition temperature, and heat capacity variation (ΔC_p) upon cooling and subsequent heating of the studied plasticizers

Sample No.	Plasti-sizer	MM, g/mol	Transition temperature,°C		ΔC_p, J/(g·K)	
			Cooling	Heating (T_g)	Cooling	Heating
1	EG	62.07	–	–	–	–
2	EGDN	152.06	–	–	–	–
3	DEG	106.12	−100	−96	0.840	0.872
4	DEGDN	196.10	−89	−84	0.680	0.814
5	TEG	150.17	−98	−90	0.867	0.911
6	TEGDN	240.16	−84	−78	0.810	0.943
7	1,2-PG	76.09	−108	−103	0.620	0.767
8	1,2-PGDN	166.06	−104	−97	0.613	0.603
9	EPG	120.08	−89	−83	0.770	0.798
10	EPGDN	210.12	−93	−87	0.750	0.716
11	DPG	134.09	−80	−73	0.670	0.704
12	DPGDN	224.14	−94	−90	0.603	0.601

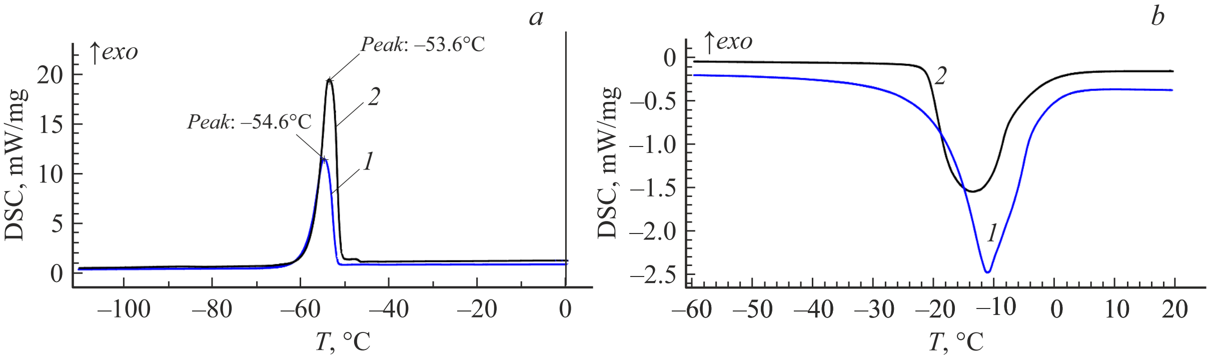

Figure 1. DSC curves of samples Nos. 1 and 2 under cooling (*a*) and heating (*b*). The numbers next to curves correspond to the numbers of samples.

is observed for them in the course of subsequent heating (Fig. 1, *b*). Melting enthalpy ΔH_m is -154.9 and -116.1 J/g, and the melting onset temperature is -20.2 and -13.7°C for samples Nos. 1 and 2, respectively.

In contrast, samples Nos. 3 and 4 do not crystallize when cooled and undergo a transition from a state of viscous flow to a glass state (Fig. 2, *a*) at a temperature of −100 and −89°C, respectively (see the table).

However, supercooled samples Nos. 3 and 4 exhibit intense exothermic effects in the process of heating above temperature T_g (see the table and Fig. 2, *b*). These effects are associated with crystallization ($\Delta H_{cr} = 72.1$ and 102.2 J/g) at a temperature of −47 and −26°C, respectively. An endothermic effect driven by melting is observed in the course of further heating. The values of ΔH_m for samples Nos. 3 and 4 are -112.6 and -105.8 J/g, respectively. Higher MM values and degrees of branching are the reasons why these samples differ in their behavior from samples Nos. 1 and 2 and do not crystallize at the cooling stage. The crystallization and melting of supercooled samples Nos. 3 and 4 in the process of heating from −140 to 25°C is a characteristic feature of these compounds.

The other diols and their dinitrates (samples Nos. 5–12) are characterized only by transition temperatures under both cooling and heating (T_g; see Fig. 3).

The transitions of all samples are characterized by a heat capacity variation within the range of 0.603–0.867 J/(g·K) (under cooling) and 0.601–0.943 J/(g·K) (under heating). It should be noted that samples Nos. 7 and 8 do not crystallize and melt even in the process of heating from a supercooled state; apparently, this is attributable to their structure and the presence of a methyl group in their molecules. In addition, diol samples Nos. 9 and 11 differ from the other studied diols in that they have higher glass transition temperatures than their dinitrates (samples Nos. 10 and 12; see the table).

Thus, low-temperature characteristics of plasticizers based on ethylene glycol and their dinitrates were examined by DSC. It was demonstrated that ethylene glycol and ethylene glycol dinitrate crystallize and do not undergo a transition to a glass state. Diethylene glycol and its dinitrate do not crystallize when cooled and undergo a transition from a state of viscous flow to a glass state. Subjected to heating from the supercooled state, DEG and DEGDN are characterized by a certain glass transition temperature, but

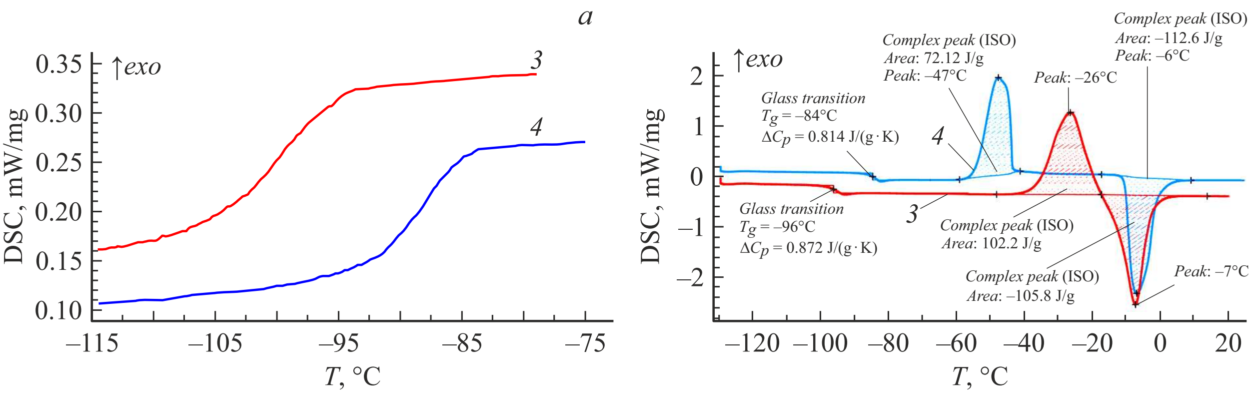

Figure 2. DSC curves of samples Nos. 3 and 4 under cooling (*a*) and heating (*b*). The numbers next to curves correspond to the numbers of samples.

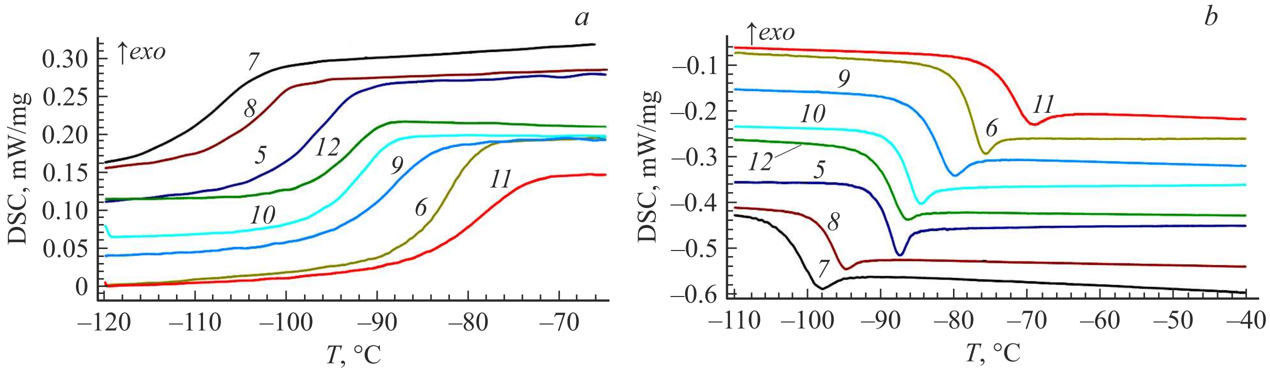

Figure 3. DSC curves of samples Nos. 5–12 under cooling (*a*) and heating (*b*). The numbers next to curves correspond to the numbers of samples.

crystallize with subsequent melting when heated further. The other diols (TEG, 1,2-PG, EPG, and DPG) and their dinitrates (TEGDN, 1,2-PGDN, EPGDN, and DPGDN) feature only transitions from a state of viscous flow to a glass state (under cooling) and back (under heating) without crystallization and melting.

Conflict of interest

The authors declare that they have no conflict of interest.

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