Thermal, glass-forming, nonlinear optical and holographic properties of "push-pull" type azochromophores with triphenyl moieties containing isophorene and pyranylidene fragments

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ABSTRACT

Molecular organic compounds with electron donating fragment bounded through π-conjugated system with electron acceptor fragment, as well as with incorporated triphenyl groups in their molecules show potential for creating cheap and simple solution processable materials with nonlinear optical properties. Additional insertion of azobenzene fragment in their structures makes them also possible to form holographic volume and surface relief gratings (SRG) after exposure to laser radiation, which could be useful for holographic data storage. For these purposes polymers are generally used. However, their application is complicated and challenging task as in every attempt to obtain the same polymer it will have different physical properties. On the other hand, the synthetic procedure of molecular glasses is more simple as their structure and physical properties are strongly defined. Unfortunately, there is still no clear relation between compound organic structures and their thermal, glass-forming and optical properties.

In order to investigate the above mentioned regularities, we have synthesized and investigated ten molecular glassy organic compounds with three different fragments as main backbones of the molecules: indene-1,3-dione (WE-1, WE-2, WE-3), isophorene (IWK-1D, IWK-2M, IWK-2D) and pyranylidene (DWK-2TB, ZWK-2TB, JWK-2TB, ZWK-3AZO). Compounds containing isophorene fragment in their molecules had the highest NLO efficiencies (d_{33} up to 125.7 pm/V for IWK-2D) and also were the most effective holographic data storage compounds with holographic self diffraction efficiency 13% and holographic diffraction efficiency 20%, also for IWK-2D, but their thermal stability (T_d from 288°C to 295°C) and glass transition (T_g from 90°C to 105°C) values were just average. Pyranylidene type compounds had the highest thermal stability and highest glass transition (T_g from 115°C to 180°C). But their ability to form and maintain amorphous structure were low and they had average NLO efficiencies (d_{33} up to 66.2 pm/V for ZWK-2TB) and average holographic self diffraction efficiency 2% and holographic diffraction efficiency 8% for ZWK-3AZO. The molecules with just azobenzene fragment and indene-1,3-dione as electron acceptor has the lowest thermal (T_d from 250°C to 282°C, T_g from 70°C to 98°C) and also the lowest holographic properties with holographic diffraction and self diffraction efficiencies at 4% for WE-1 and lower for other compounds. Nevertheless, some of the investigated molecular glasses show potential as multifunctional optical materials.

Keywords: Molecular glasses, SRG, NLO, holographic gratings, azobenzene, isophorene, pyranylidene

1. INTRODUCTION

In the last decade the organic compounds with electron donating fragment bounded through π-conjugated system with electron acceptor fragment in their molecules have attracted considerable attention of scientists due to their potential applications as optical materials - such as materials for nonlinear optics (NLO) and materials for holographic data storage. Comparing to inorganic crystals, which were already used for this purpose, the organic materials obtained in synthesis are flexible, light and have low-cost fabrication possibility[1]. Many different small organic molecules with the above mentioned optical properties have been synthesized an investigated[1-5].

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To enable the low-cost optical device fabrication opportunity, the already described small organic molecules been either attached to the main or side chain of the polymers[1, 6-7], or mixed into a polymer matrix creating a "host-guest" system[1, 8-10]. However their application is complicated and challenging task as in every attempt to obtain the same polymer it will have different physical properties. The another disadvantage is the inert volume of the material which is composed from the active chromophore part and the larger glass-forming polymer part[1]. Lastly, the phase separation problem might occur in the polymer composites with too high concentration of the chromophores[1, 9].

In our previous researches[11-13] we have discovered, that incorporating triphenyl groups in the low molecular mass organic molecules enables their excellent solubility in non-polar organic solvents and are able to form good optical quality glassy films without mixing in a polymer matrix. Such materials with nonlinear optical activity[11], light-emitting[12-13] and amplified spontaneous emission properties[14-15] have been synthesized and investigated by us. Additional insertion of azobenzene fragment in their structures makes them also possible to form holographic volume and surface relief gratings (SRG) after exposure to laser radiation. This physical phenomena could be used for information and holographic data storage[16-17]. Unfortunately, there is still no clear relation between compound organic structures and their thermal, glass-forming and optical properties.

In order to investigate the above mentioned regularities, we have synthesized and investigated ten molecular glassy organic compounds with three different fragments as main backbones of the molecules: indene-1,3-dione (**WE-1**, **WE-2**, **WE-3**), isophorene (**IWK-1D**, **IWK-2M**, **IWK-2D**) and pyranylidene (**DWK-2TB**, **ZWK-2TB**, **JWK-2TB**, **ZWK-3AZO**). Our findings on their structural relation with thermal, glass-forming, nonlinear optical and holographic properties will be described in this report.

2. MATERIALS AND METHODS

Required solvents (dichloromethane and chloroform) for obtaining thin solid films from their solutions were dried by refluxing with calcium hydride and distilled. The ^{1}H-NMR spectra on investigated organic compounds were obtained on a Bruker UXNMR/XWIN-NMR spectrometer (300 MHz).

2.1 Investigated compounds

We have synthesized ten glassy organic compounds [Fig.1.] which could be grouped in three different classes with similar key molecular fragments:

1) Azobenzene group containing molecular glasses with indene-1,3-dione as electron acceptor fragment - 2-(4-((4-(Ethyl(2-(trityloxy)ethyl)amino)phenyl)diazenyl)benzylidene)-1*H*-indene-1,3(2*H*)-dione (**WE-1**), 2-(4-((4-(Bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)benzylidene)-1*H*-indene-1,3(2*H*)-dione (**WE-2**) and 2-(4-((4-(Bis(2-(triphenylsilyloxy)ethyl)amino)phenyl)diazenyl)benzylidene)-1*H*-indene-1,3(2*H*)-dione (**WE-3**). They have been synthesized in our previous research[16] . These materials differ only by number and type of amorphous phase creating functional groups in the molecules. Compound **WE-1** contain just one trityloxyethyl group while **WE-2** has two such fragments. **WE-3** has two triphenylsilyl groups where two carbon atoms are substituted with silicon.

2) Isophorene fragment containing "push-pull" type molecular glasses - 2-(3-(4-(Bis(2-(trityloxy)ethyl)amino)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (**IWK-1D**), 2-(3-(4-((4-(Ethyl(2-(trityloxy)ethyl)amino)phenyl)diazenyl)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (**IWK-2M**) and 2-(3-(4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (**IWK-2D**). Compound **IWK-1D** been synthesized as in our previous research[18]. Compounds **IWK-2M** and **IWK-2D** have been synthesized similar as **IWK-1D** from reactants obtained previously by us[16,18]. Compound **IWK-1D** contains two trityloxyethyl fragments but does NOT contain azophenyl group. However, both other compounds - **IWK-2M** and **IWK-2D** contain the missing azobenzene fragment, but **IWK-2M** has one trityloxyethyl group while **IWK-2D** has two such fragments.

3) Pyranylidene fragment containing "push-pull" type azochromophores - 2-(2-(4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)styryl)-6-tert-butyl-4*H*-pyran-4-ylidene)-1*H*-indene-1,3(2*H*)-dione (**ZWK-2TB**), 2-(2-(4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)styryl)-6-tert-butyl-4*H*-pyran-4-ylidene)malononitrile (**DWK-2TB**), 5-(2-(4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)styryl)-6-tert-

butyl-4*H*-pyran-4-ylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**JWK-2TB**) and 2-(2-(4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)styryl)-6-styryl-4*H*-pyran-4-ylidene)-1*H*-indene-1,3(2*H*)-dione (**ZWK-3AZO**). Compounds **ZWK-2TB**, **DWK-2TB**, **JWK-2TB** and **ZWK-3AZO** have been synthesized from reactants obtained previously by us[13,16, 19]. The materials **ZWK-2TB**, **DWK-2TB** and **JWK-2TB** differ only by different electron acceptor groups in the molecules - malononitrile for **DWK-2TB**, indene-1,3-dione for **ZWK-2TB** and barbituric acid for **JWK-2TB**. Both compounds - **ZWK-2TB** and **ZWK-3AZO** have indene-1,3-dione as electron acceptor part in their structures. However, **ZWK-2TB** contain *tert*-butyl group, while in case of **ZWK-3AZO** it is substituted with styryl group.

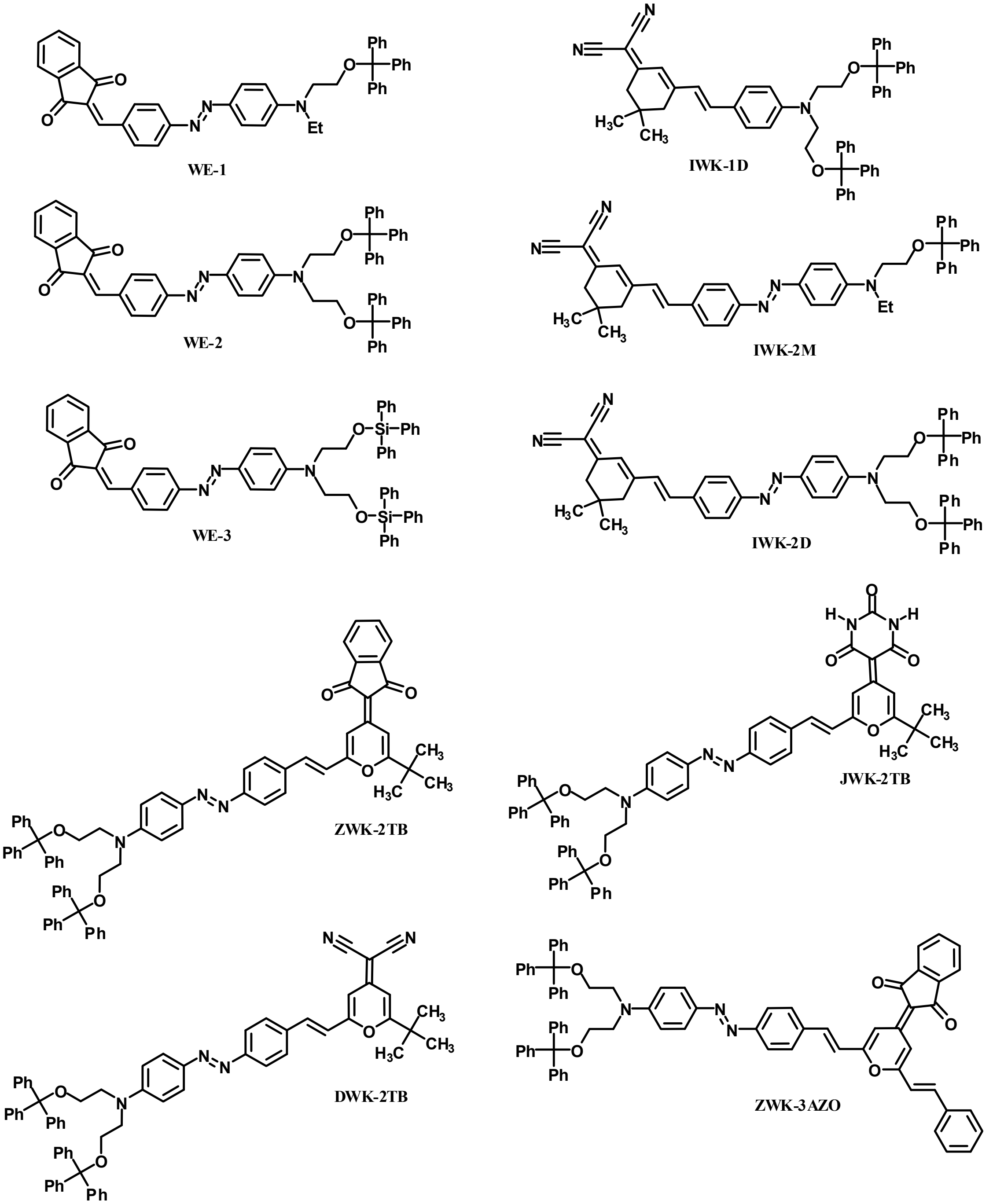

Figure 1. Investigated low-molecular mass and glass-forming organic compounds

2.2 Sample preparations for optical characterization

For absorption measurements in the solution, the investigated compounds were dissolved in dichloromethane at 10^{-5} M concentration. For absorption determination in the solid state, thin films were deposited on quartz glass by spin-coating technique. Before the deposition of the layers, the quartz glass substrates were cleaned in dichloromethane. The compound saturated solutions of dichloromethane were spin-coated on glass substrates for 40 s at 1000 rpm and 1000 rpm/s acceleration. For nonlinear optical property investigation, the films from their diluted solution of chloroform were spin-coated with a Laurell WS-400B-NPP/LITE spin-coater on indium tin oxide covered glass substrates. For holographic property determination, the investigated compounds were spin-coated on glass substrates for 120 s at 200 rpm and 500 rpm/s acceleration from their saturated solutions in chloroform.

2.3 Measurement systems

Differential scanning calorimetry (DSC) measurements were carried out by using Mettler Toledo DSC 1/200W equipment under nitrogen atmosphere and Simultaneous Thermal Analyzer STA 6000. Thermogravimetric analysis (TGA) measurements were made by using Simultaneous Thermal Analyzer STA 6000.

Absorption spectra of the compounds in dichloromethane solution were measured by Perkin Elmer Lamda 35 spectrometer. Absorption spectra of the thin films were measured by an Ocean Optics HR4000 spectrometer.

Holographic gratings with the period of 2 μm were recorder by KLASTECH DENICAFC 532-300 diode pumped solid state laser (λ=532 nm). The holographic grating readout were carried out with Melles Griot 25LH928-230 He-Ne gas laser (λ=632.8 nm). Linear p-p recording beam light polarizations were used for our experiments.

All optical measurements were carried out in ambient atmosphere at room temperature.

3. RESULTS AND DISCUSSION

3.1 Thermal properties

The thermal property measurements were carried out according to the procedures reported in our previous researches[12-13]. TGA measurement results of the compounds are shown in Fig.2. Changes in mass relative to starting mass were determined in the temperature range from +30°C to +510°C at a heating rate of 10°C/min. The T_d values were taken at the level of 5% weight loss. The most thermally stable compound - **DWK-2TB** with T_d=320°C contain pyranylidene fragment in its molecule along with malononitrile as electron acceptor group. Isophorene fragment containing compounds - **IWK-1D**, **IWK-2M** and **IWK-2D** thermal stability is similar with the other azochromophores with pyranylidene groups - **ZWK-2TB**, **JWK-2TB** and **ZWK-3AZO** with T_d from 288°C to 298°C. The least thermally stable compound was **WE-1** with the T_d=250°C. Nevertheless, the thermal stability of azochromophores **WE-2** and **WE-3** who have similar structure as **WE-1** are higher by 30°C to 32°C. The reason of such rapid chance of thermal stability for azobenzene group containing molecular glasses with indene-1,3-dione as electron acceptor fragment (**WE-1**, **WE-2**, **WE-3**) is most likely the number of triphenyl groups in the molecules. At the same time the number of triphenyl groups in the molecules containing isophorene fragment (**IWK-2M**, **IWK-2D**) do not influence their thermal stability.

The DSC measurements of the investigated compounds were carried out as described in[12,15] and are summarized in Fig.3. From all of the investigated compounds the **JWK-2TB** has the highest glass transition (T_g) value - 180°C. Comparing with pyranylidene fragment containing compounds **ZWK-2TB** and **DWK-2TB** which have similar structure - their T_g values are 120°C and 115°C. Such high difference could be explained by the hydrogen bond formation between the **JWK-2TB** molecules from pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione electron acceptor fragment. Compounds **ZWK-2TB** and **ZWK-3AZO** both have also similar structures. However for **ZWK-3AZO** the T_g=176°C while **ZWK-2TB** it is 120°C. The T_g values of isophorene fragment containing compounds (**IWK-1D**, **IWK-2M**, **IWK-2D**) are lower than for pyranylidene and are in range from 90°C to 105°C. The T_g value increases by the number of triphenylmethyl groups and additional insertion of azophenyl fragment in the molecules. Glasses **WE-1**, **WE-2** and **WE-3** had lowest T_g values (from 70°C to 98°C). Same relation as for isophorene containing glasses was observed - the T_g increases with additional incorporation of triphenylmethyl groups in the molecule. However, **WE-3** containing triphenylsilil groups had lower T_g values by 23°C comparing to **WE-2** containing triphenylmethyl groups while both having almost identical chemical structures.

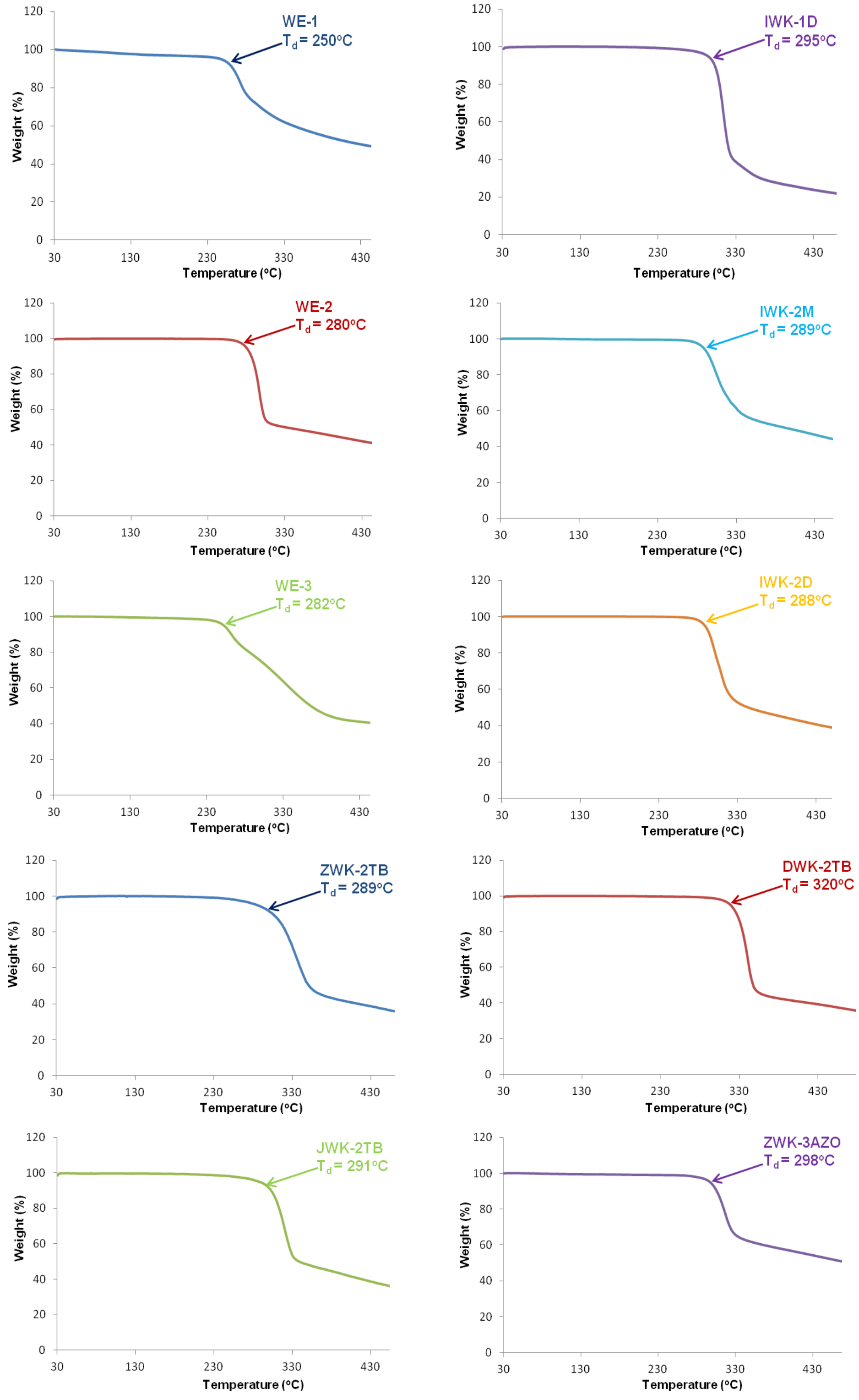

Figure 2. Thermogravimetric analysis of the investigated compounds

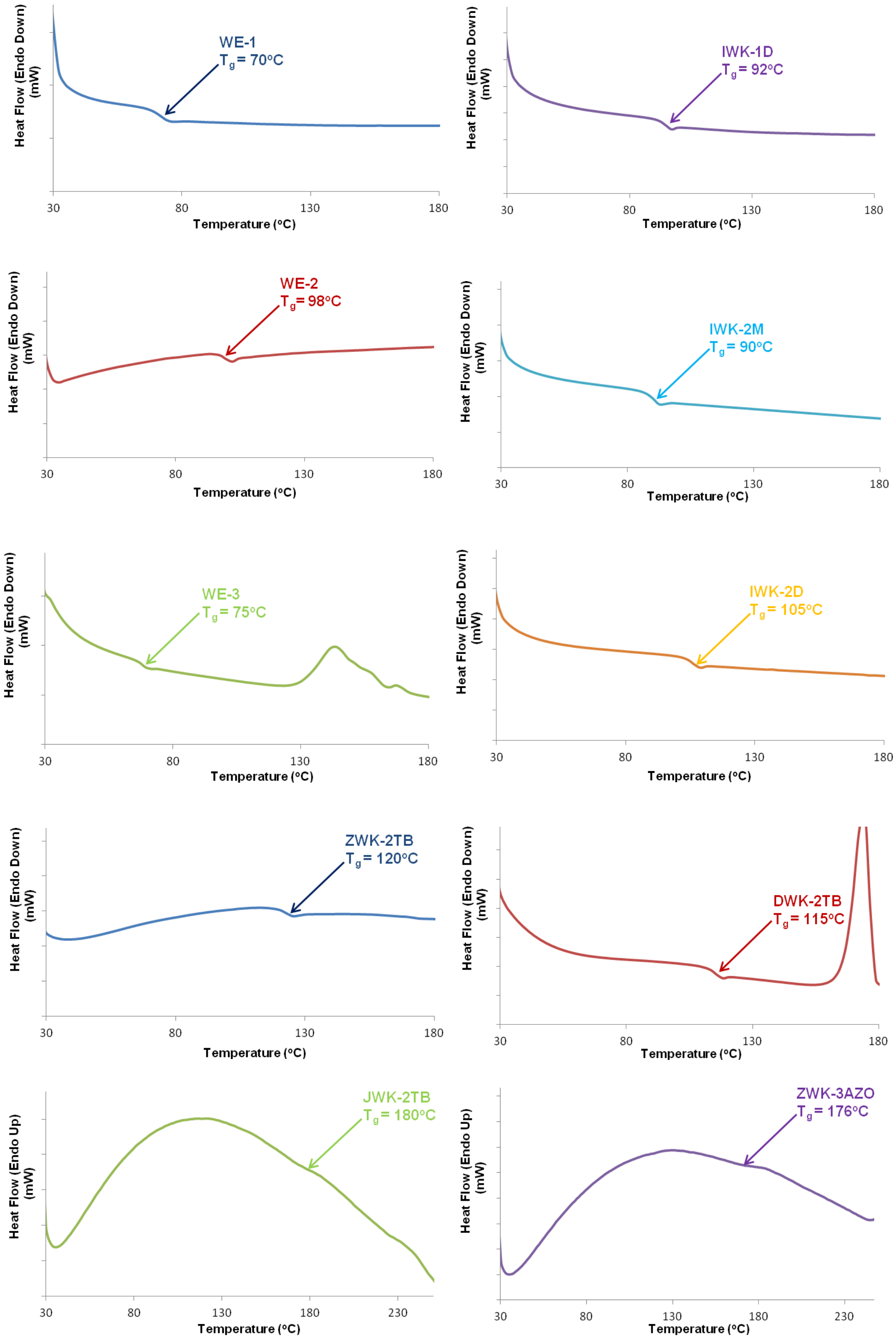

Figure 3. DSC thermogramms of the investigated compounds

3.2 Glass-forming properties

The surface of the prepared spin-coated films of the investigated compounds on the glass substrate were observed by the optical microscope Nikon Eclispe 150L. The obtained images are shown in [Fig.4.].

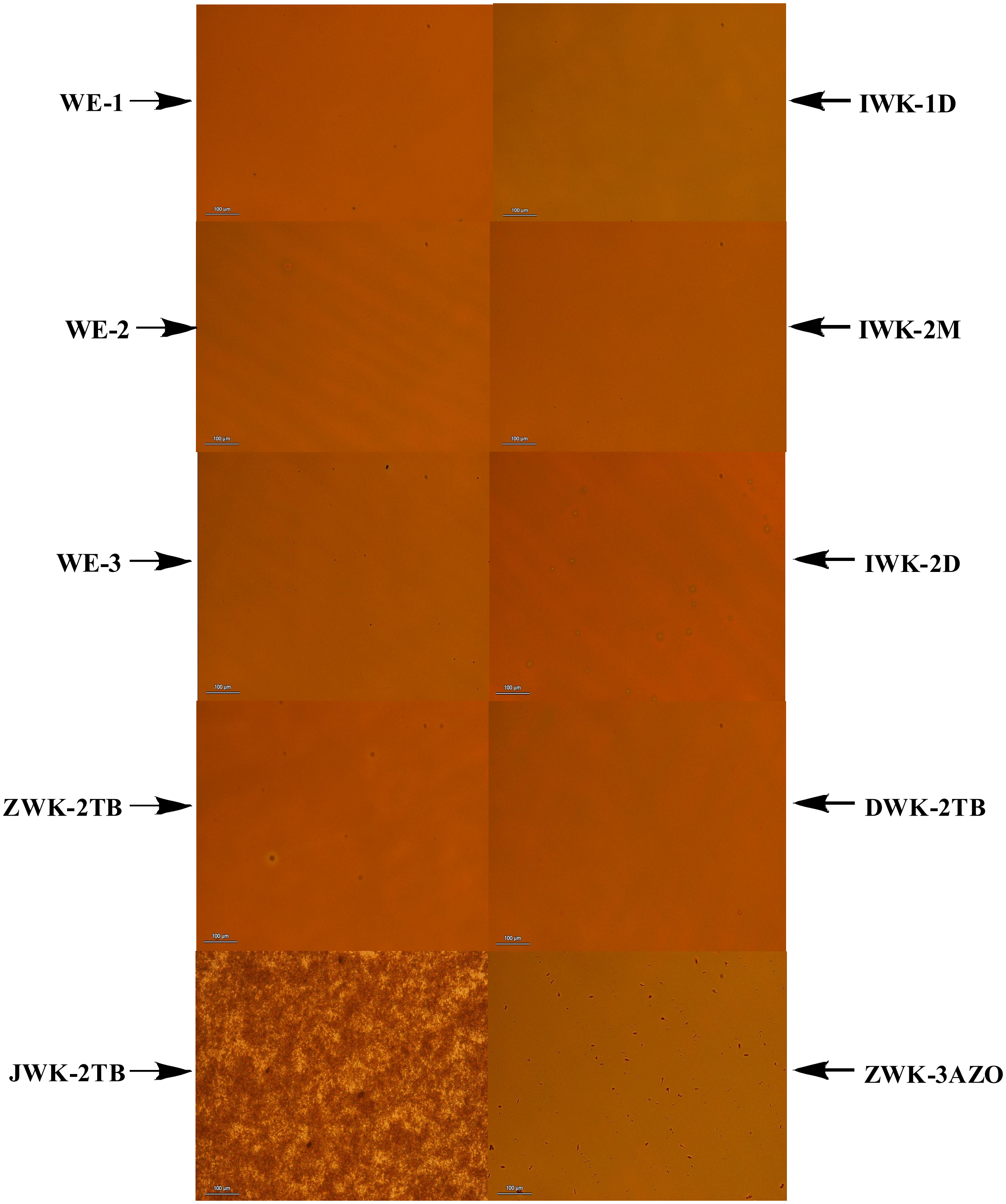

Figure 4. Optical microscope images of the pure films of the investigated compounds. Dots on the neat film surface represent compound crystalline state while the rest smooth area shows amorphous solid state.

Glasses **WE-1**, **WE-2**, **WE-3**, **IWK-1D**, **IWK-2M**, **IWK-2D**, **ZWK-2TB** and **DWK-2TB** show very small crystalline state areas in their pure films. However, the pure film obtained from compound **JWK-2TB** is full of crystals which could be caused by too strong interaction of molecules caused by already mentioned hydrogen bonds in the electron acceptor part of the molecule. Film obtained from **ZWK-3AZO** have more crystal formations, but also has lot of amorphous area. The reason for increased crystalline state in this molecule could be explained by the possible formation of dimers. The glass-forming properties of the all investigated compounds with the exception of **JWK-2TB** could be still increased by adding some polymer matrix to the compound before the preparation of the neat films.

3.3 Optical properties

For the further measurement of nonlinear optical and holographic properties of ALL investigated compounds, it was required to measure their absorption properties in solutions of dichloromethane and thin solid films. The results of these measurements are shown in Fig.5. and Fig.6.

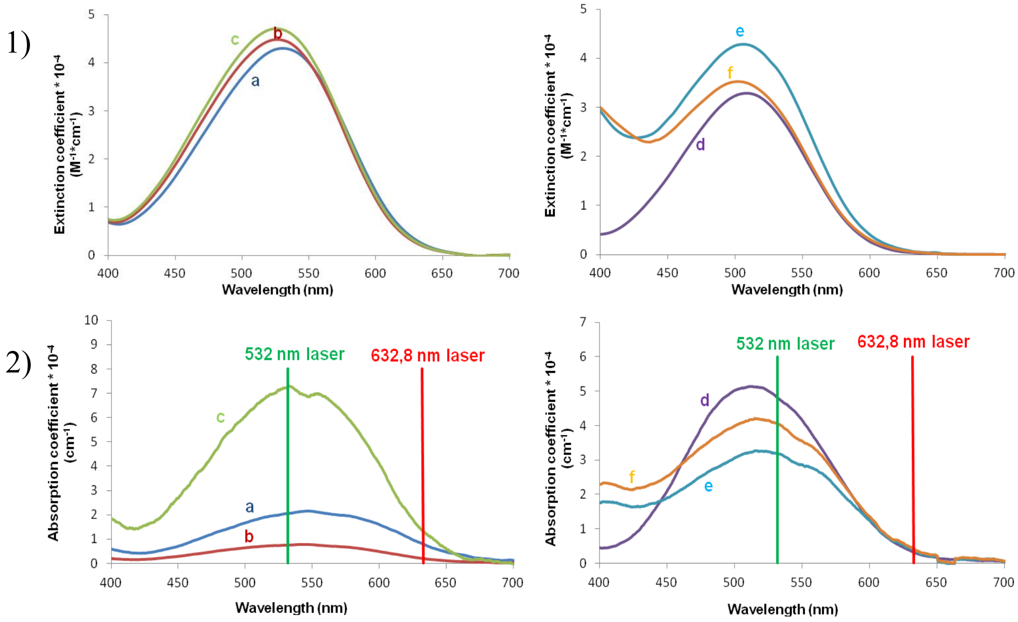

Figure 5. Absorption spectra of compounds in

1) Solution of dichloromethane and 2) Pure spin-coated films

a) WE-1, b) WE-2, c) WE-3, d) IWK-1D, e) IWK-2M, f) IWK-2D

The absorption maxima of all investigated compounds in the solid state (from 490nm to 540nm) is red-shifted by 10-20nm from their solutions of dichloromethane (from 480nm to 520nm). For glasses containing pyranylidene fragment in the molecule (**ZWK-2TB**, **DWK-2TB** and **ZWK-3AZO**) their absorption is blue-shifted by 10-20 nm comparing with molecules **WE-1**, **WE-2**, **WE-3**, **IWK-1D**, **IWK-2M** and **IWK-2D**. It could be attributed to the additional small conjugation caused by the oxygen and the double bond in the molecules of **ZWK-2TB**, **DWK-2TB** and **ZWK-3AZO** which causes a hipsochromic shift of the absorption. Due to the poor glass-forming properties [Fig.4.] we were unable to obtain the absolute absorption in neat film for **JWK-2TB**. Nevertheless, since the absorption of almost all of the investigated compounds of the pure films is close to 532nm, we could use the laser with such wavelength for holographic recording in our next experiments. Investigated compounds still had some absorption at 632.8nm so a laser with the already mentioned wavelength could be used for the readout for the obtained surface relief gratings and holographic properties.

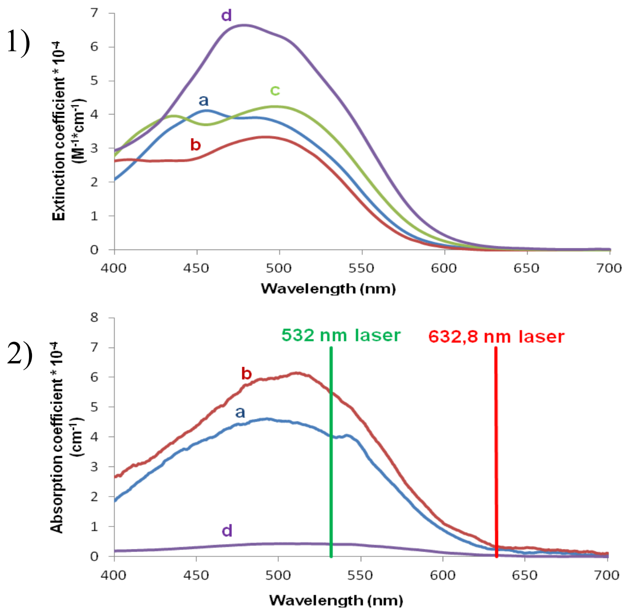

Figure 6. Absorption spectra of compounds in

1) Solution of dichloromethane and 2) Pure spin-coated films

a) ZWK-2TB, b) DWK-2TB, c) JWK-2TB, d) ZWK-3AZO

3.4 Nonlinear optical properties

The preparation of the samples and optical measurements were carried out as described in our previous researches[9,11,20].

Despite the good glass-forming properties of the compounds **WE-1**, **WE-2**, **WE-3**, **DWK-2TB** and **ZWK-3AZO** on the glass-surface, their obtained pure films on ITO glass start to crystallize upon the orientation. Therefore we were unable to determine their nonlinear properties. However we have obtained excellent pure films from compounds **IWK-1D**, **IWK-2M**, **IWK-2D** and **ZWK-2TB** on ITO glass and measured their nonlinear properties which are summarized in table 1.

Table 1. Nonlinear optical properties of thin films of compounds **IWK-1D, IWK-2M**, **IWK-2D** and **ZWK-2TB**.

Structure	**T_{SHI50} (°C)**	**Orientation T (°C)**	**d_{33} (532) (pm/V)**	**d_{31} (532) (pm/V)**	**d_{14} (532) (pm/V)**	**d33 (0) (pm/V)**
IWK-1D	76	80	98.8	55.9	50.4	2.23
IWK-2M	74	78	62.8	40.6	35.3	2.84
IWK-2D	84	90	125.7	75.4	48.4	6.05
ZWK-2TB	100	108	66.2	28.7	19.9	7.34

The nonlinear optical coefficients d_{33}, d_{31} and d_{14} are higher for isophorene type glasses (**IWK-1D**, **IWK-2M**, **IWK-2D**) then compounds containing pyranylidene fragment (**ZWK-2TB**). However, the temperature of 50% NLO intensity decay T_{SHI50} value is higher for **ZWK-2TB** by 25°C to 15°C comparing to **IWK-1D**, **IWK-2M** and **IWK-2D**. From isophorene fragment containing glasses, the compound **IWK-2D** showed the highest NLO efficiency values and highest thermal characteristics. The reason for it could be the incorporation of two triphenylmethyl groups in the molecule which enhances the orientation of the molecules in their pure films before the optical measurements.

3.5 Holographic properties

The holographic investigation of the thin films obtained from the compounds was carried out with the equipment and according to our previous researches[16-17]. The thickness of each film was found by using the light transmission and absorption at 632.8 nm. All samples were subjected to laser irradiation (power of both laser beams = 8.5 mW) for certain amount of time (**t, min**). Two photodiodes were used to detect diffracted beams (**SDE** and **DE**) and measure the self diffraction efficiency (**SDE$_t$**) and diffraction efficiency (**DE$_t$**). **DE$_t$** was measured with 632.8 nm laser. All results were measured in transmission mode and are shown in table 2 and table 3.

Table 2. Holographic properties of thin films of investigated compounds at 532 nm.

Sample	Thickness of film (µm)	SDE (µW)	t, min	SDEt, (%)	T, (%/s)	W$_{max}$	REF$_{max}$
WE-1	0.5	104.0	12	1.23	0.0017	196.93	0.0062
WE-2	3.9	2.0	9	0.03	< 0.0001	7680.12	< 0.0001
WE-3	0.2	20.0	6	0.24	0.0007	512.01	0.0005
IWK-1D	1.1	55.0	9	0.65	0.0012	279.28	0.0023
IWK-2M	0.9	320.0	8	3.77	0.0078	42.67	0.0882
IWK-2D	0.7	1100.0	24	12.94	0.0090	37.24	0.3475
ZWK-2TB	0.2	130.0	10	1.53	0.0026	131.29	0.0117
DWK-2TB	0.2	90.0	9	1.07	0.0020	170.67	0.0062
ZWK-3AZO	4.1	200.0	9	2.36	0.0043	76.80	0.0306

Table 3. Holographic properties of thin films of investigated compounds at 632.8 nm.

Sample	Thickness of film (µm)	DE (µW)	t, min	DEt, (%)	T, (%/s)	W$_{max}$	REF$_{max}$
WE-1	0.5	23.5	12	4.70	0.0065	4.51	1.4300
WE-2	3.9	7.0	12	1.40	0.0019	15.13	0.0930
WE-3	0.2	6.5	8	1.30	0.0027	10.86	0.1200
IWK-1D	1.1	9.7	3	1.94	0.0108	2.73	0.7109
IWK-2M	0.9	45.0	9	9.00	0.0167	1.77	5.1000
IWK-2D	0.7	102.0	24	20.40	0.0142	2.08	9.8300
ZWK-2TB	0.2	2.0	12	0.40	0.0006	52.94	0.0076
DWK-2TB	0.2	5.0	10	1.00	0.0017	17.65	0.0567
ZWK-3AZO	4.1	41.0	12	8.20	0.0112	2.58	3.1750

The samples prepared from the isophorene group containing compounds showed the highest self diffraction (13% for **IWK-2D** and almost 4% for **IWK-2M**) and diffraction (20% for **IWK-2D** and 9% for **IWK-2M**) efficiencies followed by the sample prepared by pyranylidene group containing compound **ZWK-3AZO** with 2% self diffraction efficiency and 8% diffraction efficiency and azobenzene derivate **WE-1** with 1% self diffraction efficiency and 4% diffraction efficiency. The least effective holographic data storage properties were observed for other pyranylidene fragment containing compounds **DWK-2TB**, **ZWK-2TB** and other azobenzene derivatives **WE-2**, **WE-3** with diffraction and self diffraction efficiencies about 1% and lower.

4. CONCLUSIONS

Almost all of the synthesized molecular glasses - **WE-1**, **WE-2**, **WE-3**, **IWK-1D**, **IWK-2M**, **IWK-2D**, **ZWK-2TB**, **DWK-2TB** and **ZWK-3AZO** form amorphous structure from their solutions of volatile organic solvents. All glasses show good thermal stability with thermal decomposition temperatures from 250^{o}C to 320^{o}C. The glass transition temperatures of investigated compounds are higher than 70^{o}C and even up to 180^{o}C for **JWK-2TB**. However, **JWK-2TB** showed very poor formation of amorphous structure and solubility in solutions of chloroform and dichloromethane. Although the glasses with isophorene fragment in their molecules (**IWK-1D**, **IWK-2M**, **IWK-2D**) showed just average glass transition values (from 90^{o}C to 105^{o}C), from all of them a good quality pure films on ITO glass were obtained after the orientation and they also had not only the highest NLO efficiencies (d_{33} up to 125.7 pm/V for **IWK-2D**), but also were the most effective holographic data storage materials with holographic self diffraction efficiency 13% and holographic diffraction efficiency 20%, also for **IWK-2D**, which make them perspective as potential multifunctional optical materials. Other compounds with pyranylidene fragment in their molecules (**ZWK-2TB**, **DWK-2TB**, **ZWK-3AZO**) were most thermally stable (thermal decomposition temperatures from 299^{o}C to 320^{o}C.) and had highest glass transition values (from 115^{o}C to 176^{o}C). However, not all of them had a good ability to form thin films from solutions and the highest NLO efficiency (d_{33} up to 66.2 pm/V for **ZWK-2TB** and the highest holographic self diffraction efficiency of 2% and diffraction efficiency of 8% was observed for **ZWK-3AZO**.

The least effective compounds were azobenzene derivatives **WE-1**, **WE-2**, **WE-3**. They had the lowest thermal stabilities (from 250^{o}C to 282^{o}C), lowest glass transition values (from 70^{o}C to 98^{o}C). Although they had good glass-forming properties from solution, they still were least effective holographic data storage materials (with diffraction and self diffraction efficiencies about 1% and lower) and no pure film obtained from them remained amorphous after orientation in the required experiments for NLO property determination. As we conducted from this reach, the glass transition and the thermal stability could be increased by incorporation of additional amorphous phase forming groups. However, not all of the molecules could maintain their amorphous structure in the solid state. This drawback could still be improved by adding additional glass-forming triphenyl group in the molecule or also by doping some of the synthesized molecules in a polymer matrix.

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