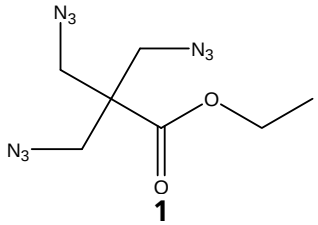
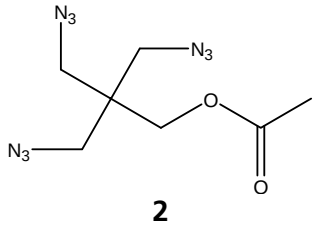
Synthesis and Characterization of New Triazido-plasticizers

G. Unkelbach, Th. Keicher, H. Krause
Fraunhofer-Institut für Chemische Technologie (ICT)
Postfach 1240, D-76327 Pfinztal, Germany

1. Abstract

Azidoplasticizers can be useful in all types of energetic systems especially when the binders have azidogroups. If plasticizer and binder comprise similar chemical type the interaction and compatibility are excellent. Another aspect is that azidoplasticizers supply additional energy to the system because such compounds have high heats of formation.
In this paper we present the synthesis and some properties of the two new compounds TAPE-E and TAP-Ac which are azidoesters and have nitrogen contents of about 50%. Both compounds have the same molecular formula but because of different position of the carboxyl group they are isomers. The influence of the different position of the carboxyl group on the resulting properties like decomposition behaviour and glass transition point is presented.

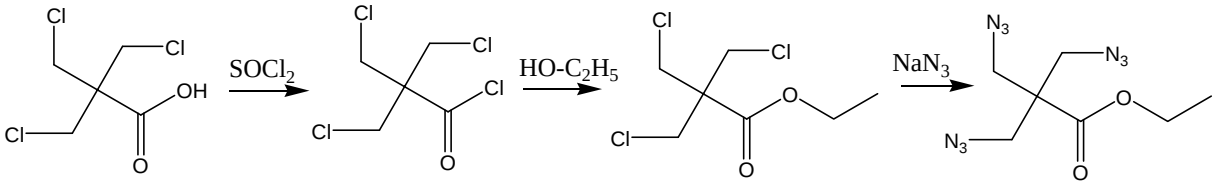
TAPE-E	**TAP-Ac**
 **1**	 **2**
Triazidopivalic-acid-ethylester	Triazidopentaerythrite-acetat

2. Results

2.1 TAPE-E

2.1.1 Synthesis of TAPE-E

TAPE-E is synthesised from Trichloropivalic-acid [1] by converting into Trichloropivaloyl-chloride [2] followed by esterfication [3] with ethanol and finally the azidation step. The first two steps of the synthesis work very well in high yields of 85 and 87% consecutively. The azidation reaction is quite slow, therefore it took 14 days at 95°C in DMF solution to achieve quantitative replacement of the halogen substituents. The azidation reaction gave TAPE-E in 70% yield as pale yellow oil. Scheme 1 shows the synthesis route.

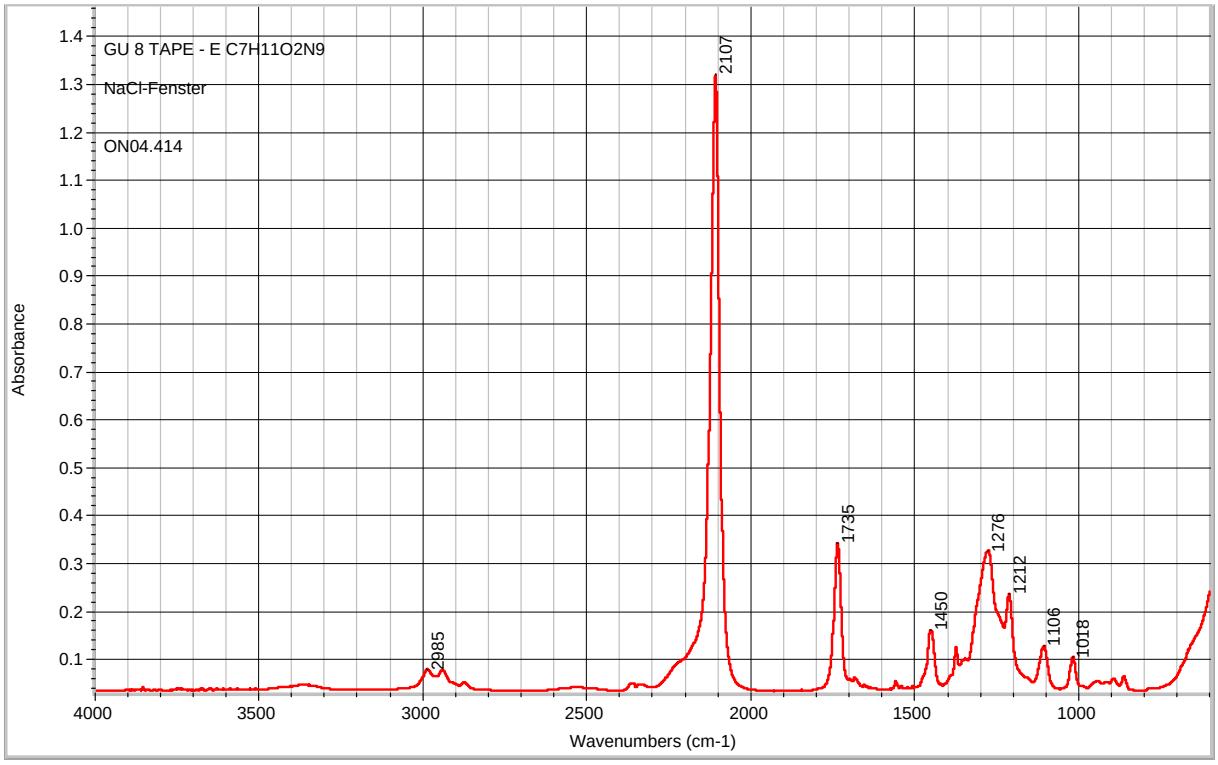


Scheme 1- Synthesis of TAPE-E

2.1.2 Spectra and DSC analysis of TAPE-E

The infrared spectrum shows the specific absorption of the ester carbonyl group at 1735 cm^{-1} and the absorption of the azide group at 2107 cm^{-1} (Fig. 1).
^{1}H-NMR (Fig. 2) of TAPE-E exhibited one singlet corresponding to methylene protons which belongs to azidomethyl group (δ = 3.56ppm) and one multiplet at 4,27-4,22ppm for the methylene group next to the carbonyl. The triplet for the methyl group is at 1,30ppm.
The DSC analysis is shown in Fig. 3.1 and 3.2. The exothermic peak from decomposition of the azide groups is observed at 221.76°C which is typical for azide compounds. The glasstransition temperature was measured between -94 to -92°C which is quite low and promises good plasticizing properties even at low temperatures. The refractive index is n_D^{20} = 1,4990

Figure 1- IR-spectra of TAPE-E



-Figure 2- ^{1}H NMR of TAPE-E

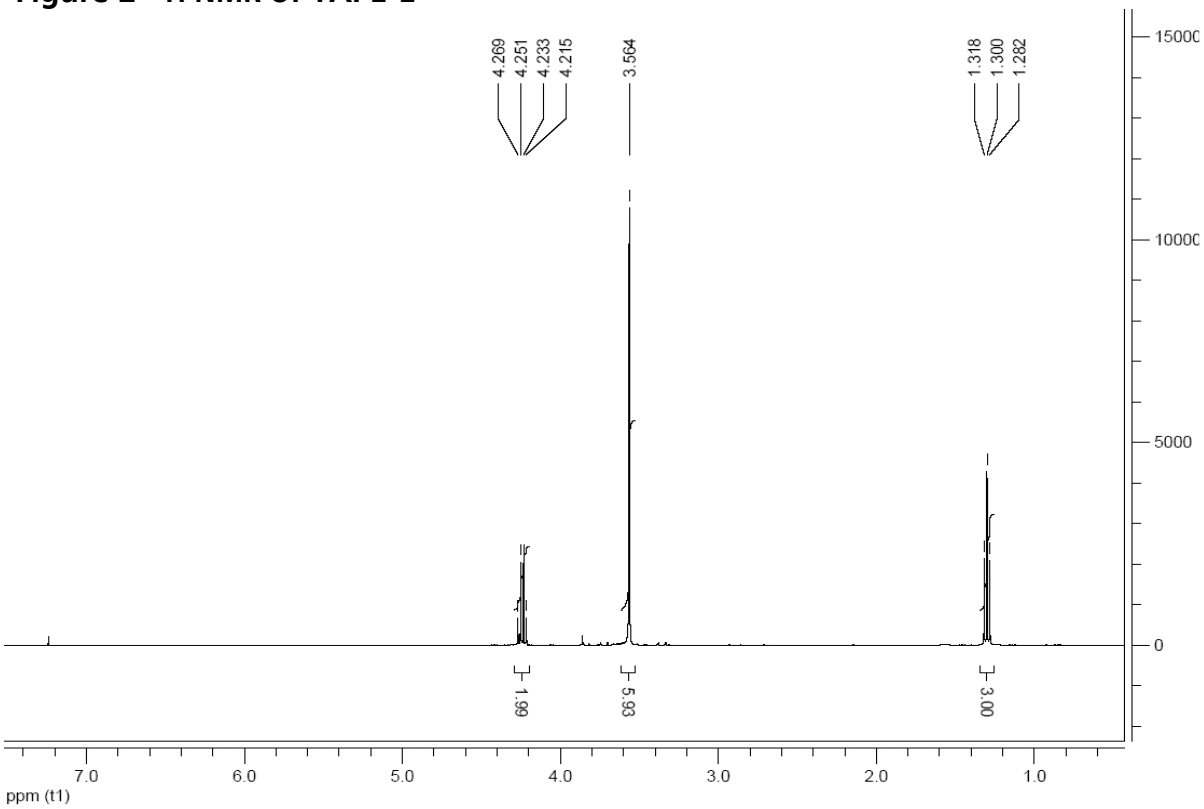


Figure 2.1- DSC of TAPE-E (Decomposition)

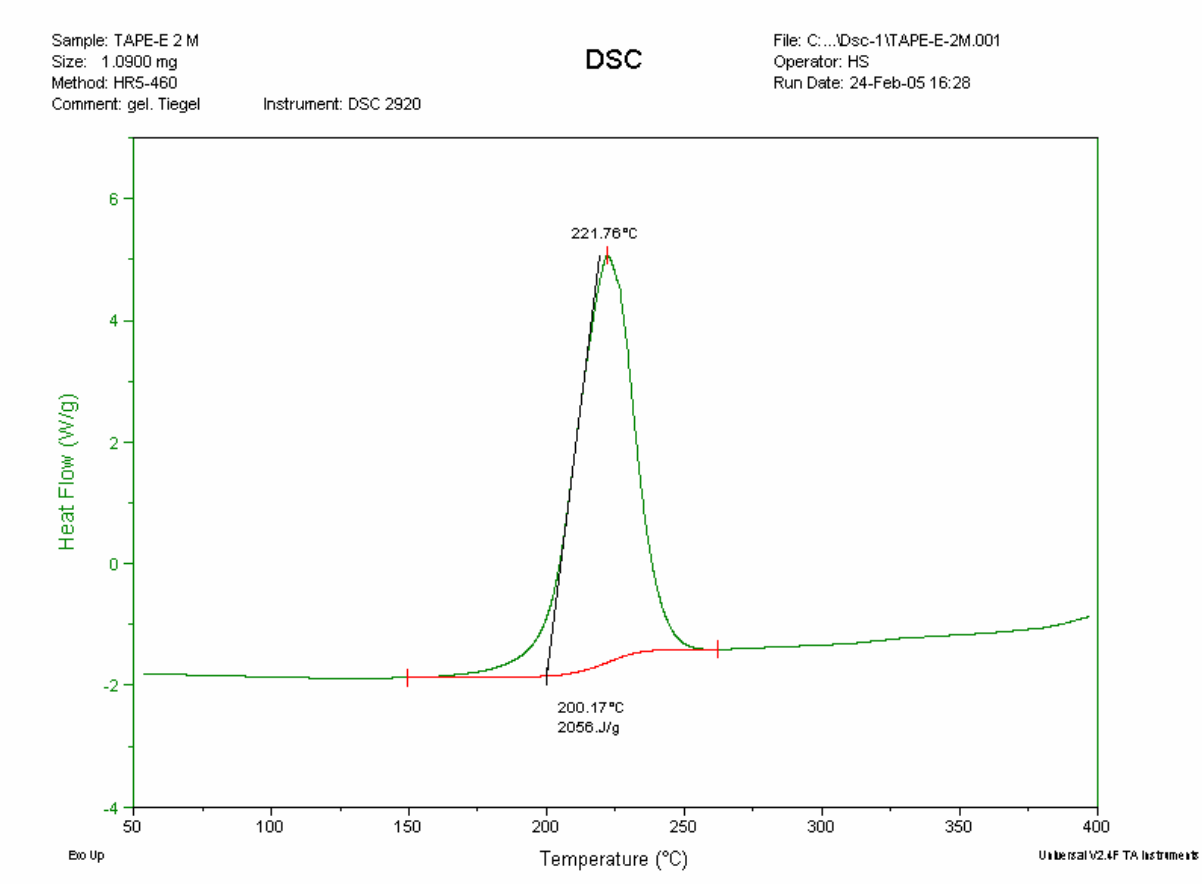
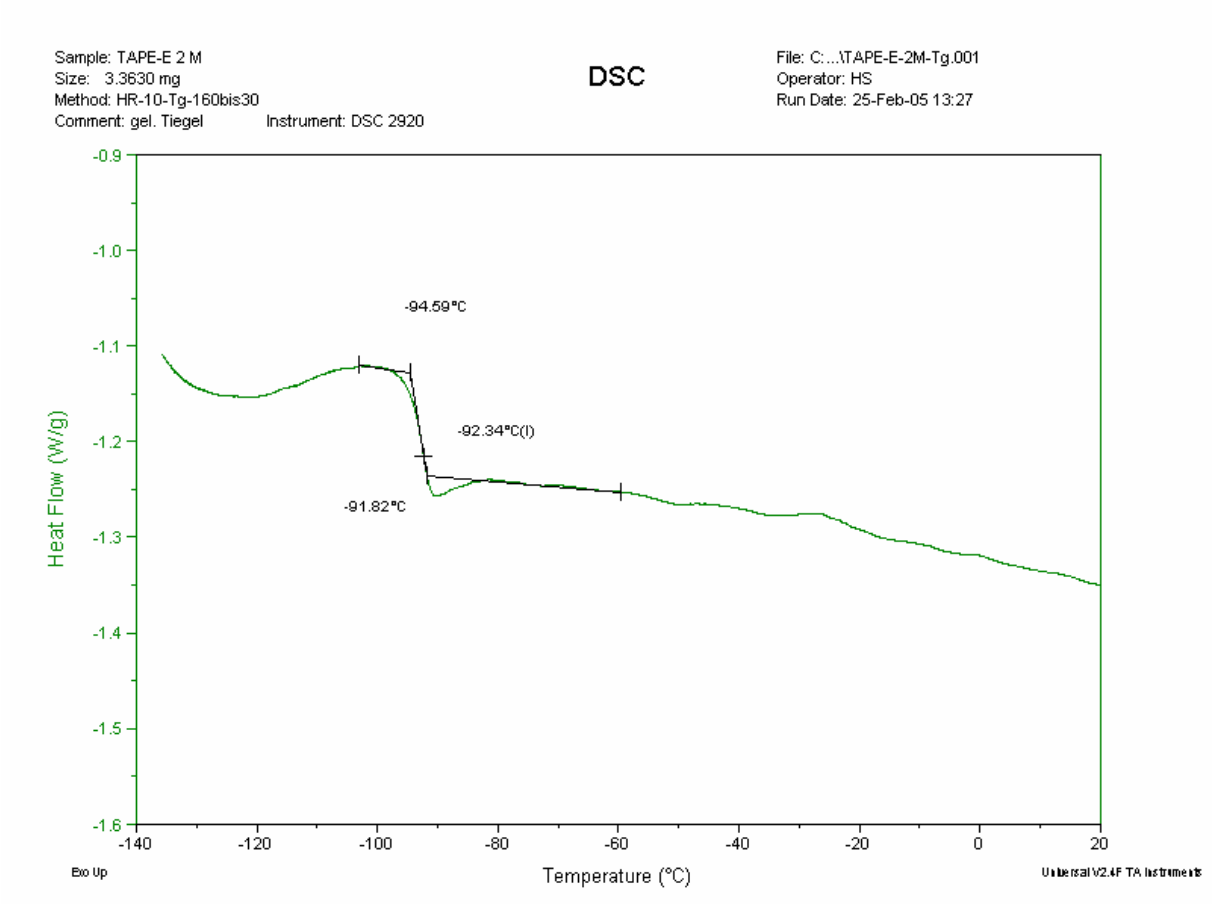


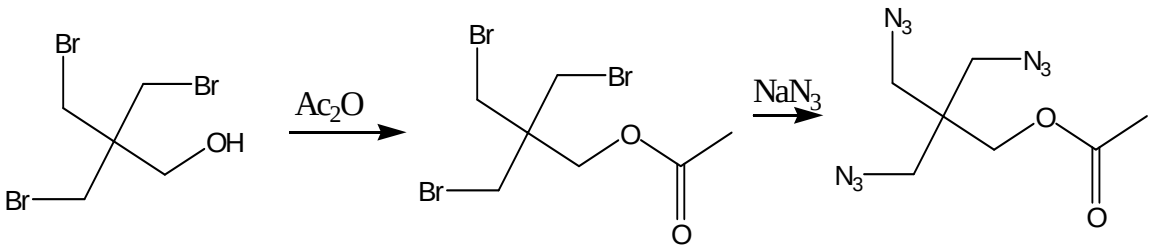
Figure 2.2- DSC of TAPE-E (Glasstransition Temperature)



2.2 TAP-Ac

2.2.1 Synthesis of TAP-Ac

The synthetic route for TAP-Ac started from tribromo-neopentyl alcohol supplied as free sample from the American Brom, Inc. of New York Company.
First tribromo-neopentyl alcohol was converted into the corresponding acetic acid ester with acetic anhydride and finally azide substituted by sodium azide (Scheme 2).



Scheme 2- Synthesis of TAP-Ac

2.2.2 Spectra and DSC analysis of TAP-Ac

The infrared spectrum shows the absorption of the ester carbonyl group at 1747 cm^{-1} and the absorption of the azide group at 2103 cm^{-1} (Fig. 3).
^{1}H-NMR (Fig. 4) of TAP-Ac shows three singlets. The methylene protons which belong to the azidomethyl groups have their peak at 3,35ppm and the methylene group next to carboxyl group has its singlet at 3,96ppm. The singlet for the methyl group is at 2,08ppm.
The decomposition temperature was measured by DSC and had its peak at 241,36°C (Fig. 5.1). The DSC curve for determination of the glasstransition temperature is shown in Fig. 5.2. The glasstransition temperature of TAP-Ac is between -86 to -83°C.
The refractive index is n_D^{20} = 1,5092.

Figure 3- IR-spectra of TAP-Ac

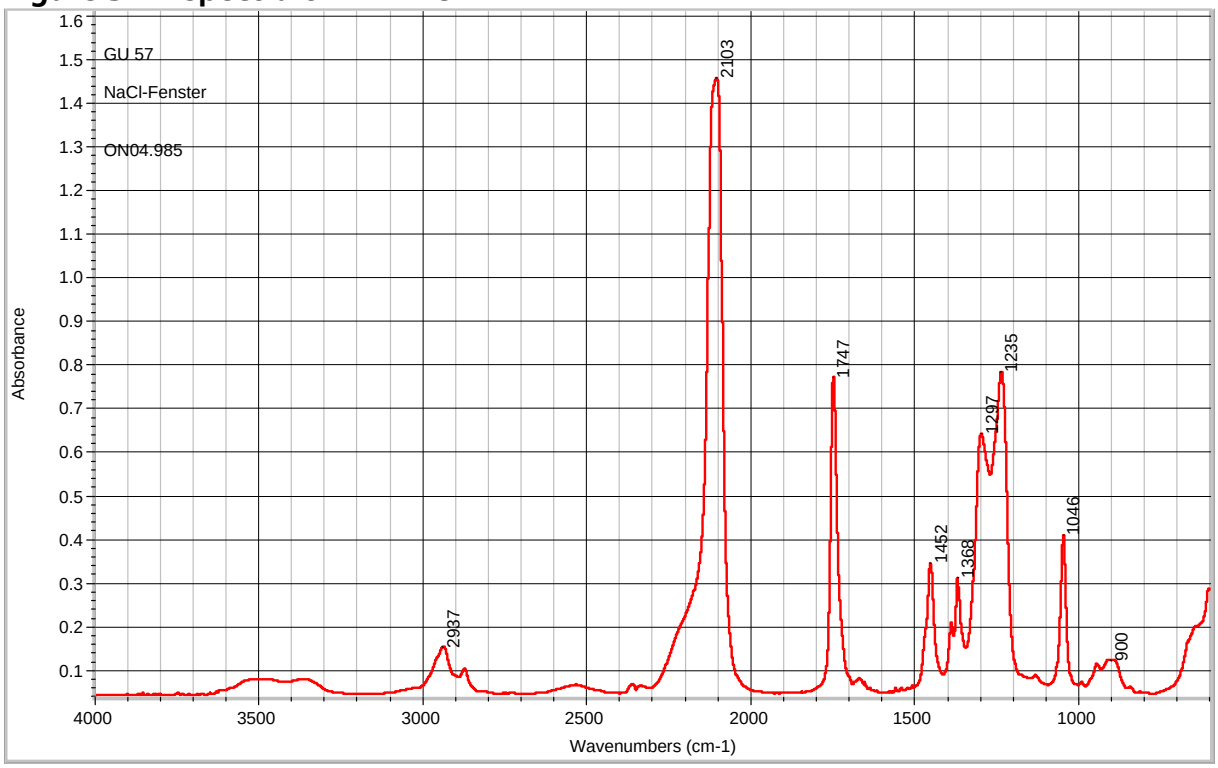


Figure 4- ^{1}H NMR of TAP-Ac

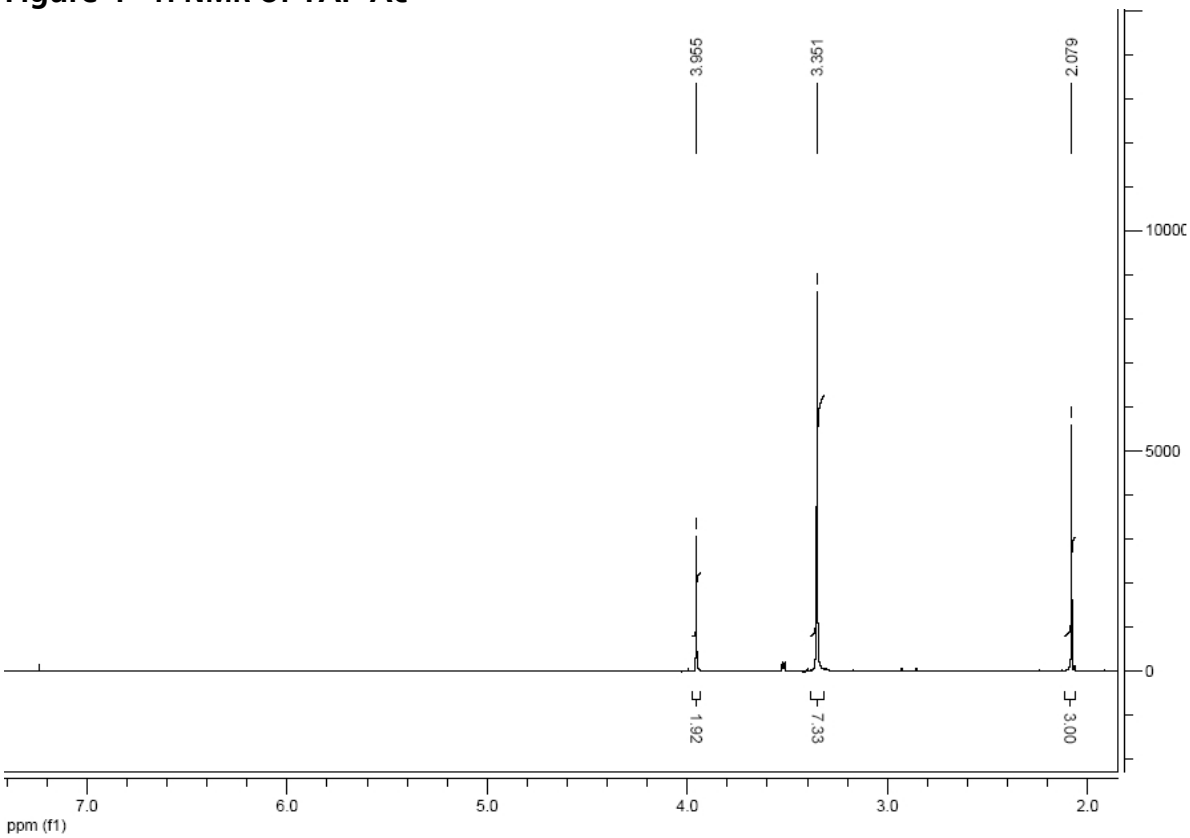


Figure 5.1- DSC of TAP-Ac (Decomposition)

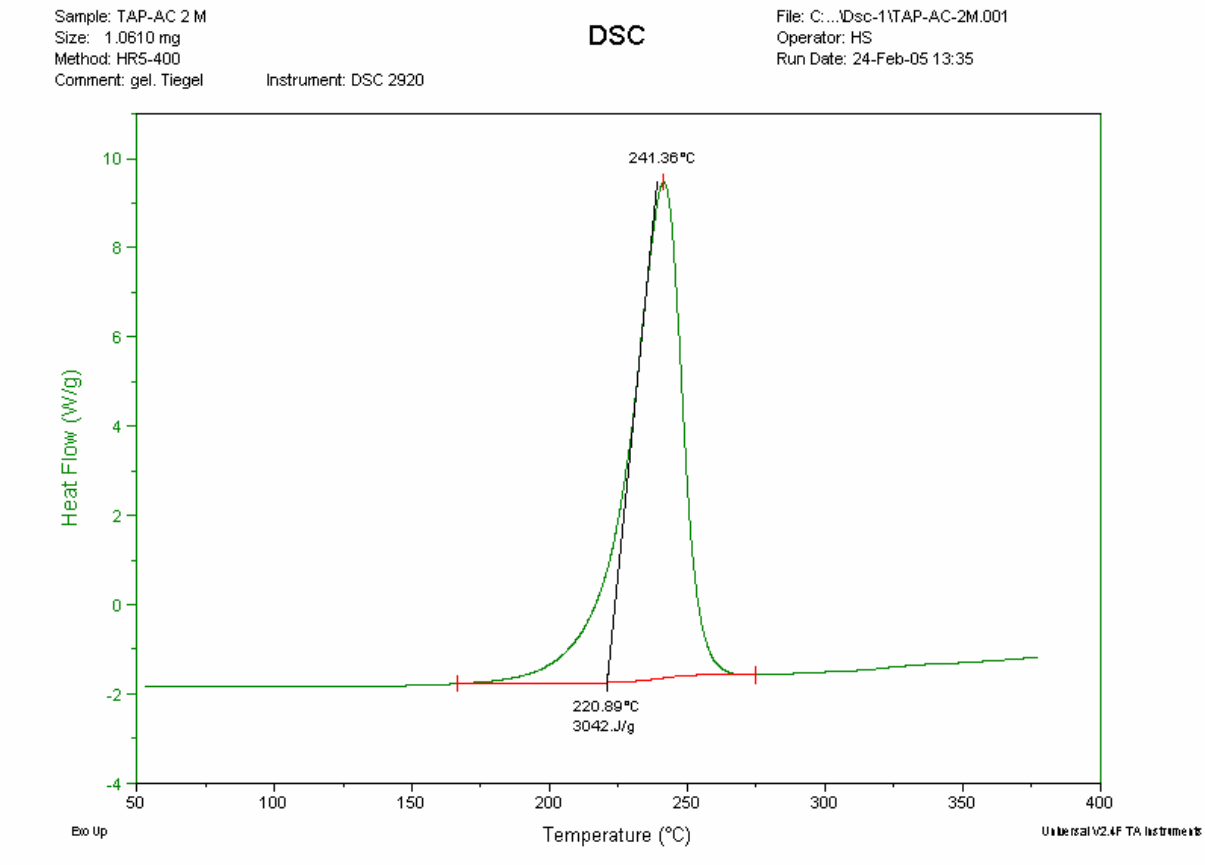
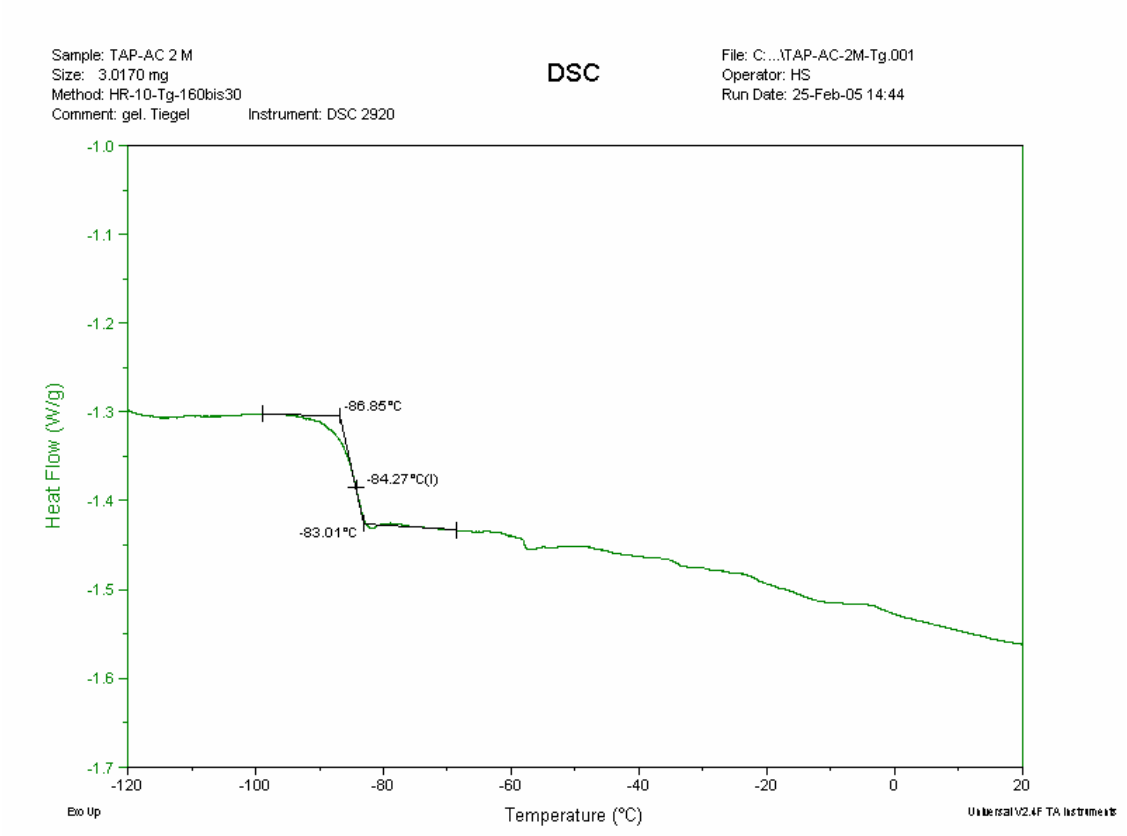


Figure 5.2- DSC of TAPE-E (Glasstransition Temperature)



2.3 Properties and Analysis of TAPE-E and TAP-Ac

Table 1 - Properties and Analysis of TAPE-E and TAP-Ac

	Density [g/cm^3]	O_2 - Balance [%]	Impact Sensitivity [Nm]	Friction Sensitivity [N]	Enthalpy of Formation [KJ/mol]	Glass-transition Temperature [°C]	Decomposit. Temperature (Peak-DSC) [°C]
TAPE-E	1,218	-110,57	1	64	502,87	-94 / -92	221
TAP-Ac	1,244	-110,57	1	54	595,36	-86 / -83	241

The density of this both plasticizers is similar and the oxygen balance is identical because these compounds are isomers with only different position of the carboxyl group. The sensitivity tests gave also very similar data for both compounds. The high nitrogen content of 49,78% is due to the azide groups and causes this high sensitivity against mechanical stimulus.
There is a significant difference of about 100 KJ/mol in the enthalpy formation of TAPE-E and TAP-Ac. A clear difference in glasstransition temperature can also be observed as TAPE-E shows 10°C lower temperature than TAP-Ac. Based on this fact we could say that the polar carboxyl group in case of TAPE-E is more shielded from inter molecular interactions then in TAP-Ac. Nevertheless both temperatures are quite low and promise good plasticizing properties even at low temperatures.
From DSC measurement TAP-Ac shows slightly higher decomposition temperatures then TAPE-E.

3. References

[1] A. Mooradian, J.B. Cloke, American Chem. Soc. Journal 67, 1945, 1/6

[2] A.N. Gafarov, T.S. Kharasova, and R.N. Minabutdinova, Deposited Manuscript No. DR-95, Informatsiya o Novykh Postupleniyakh Literatury, No. 1, 32 (1979)

[3] F. Nerdel, A. Heymons & H. Croon, Über trisubstituierte Pivalinsäuren, Chem. Ber. Band 91, 1958, S. 938 – 943