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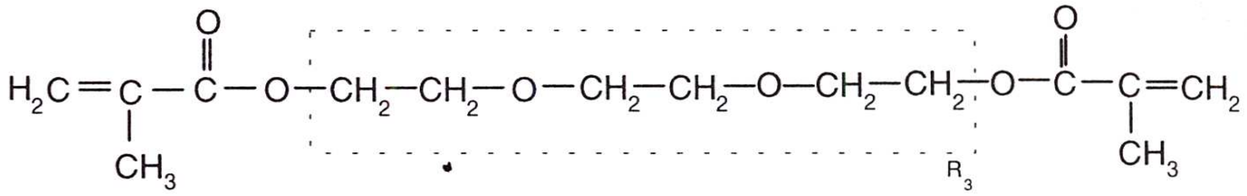
Structure and Optical Properties of TGM-3 Photopolymer

I. Introduction

Still increasing interest in the photopolymers based on oligoether(meth)acrylates (OGM) was recently observed [1-3] because of their possible use in optoelectronics, holography and typography materials engineering. These materials are often better than traditional photopolymers (e.g., polyurethane) taking into consideration their mechanical (elastic) as well as piezooptical and optical transparency properties. The TGM-3 is one of the oligoether(meth)acrylates. It would be very important to study its fundamental physical properties, e.g. a molecular structure, a charge distribution or one-electron energies in order to understand observed behaviour of the more complex photopolymer compositions.

In our previous work [4] we have reported a low-temperature anomaly of optical second harmonic generation (SHG) that corresponds to occurrence of a low-temperature structure reorientation in such materials. The anomalies were previously investigated using acoustooptical methods because the latter are very sensitive to changes of the optical as well as the elastic parameters.

Chemical formula of the TGM-3 molecule is presented below according to our previous investigations [4] :



$$H_2C=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-\underbrace{CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2}_{R_3}-O-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2$$

The solid many-component photopolymers are usually obtained by a proper light illumination using a UV-hydrogen lamp with different exposure times. Our previous investigations have shown that optimum exposure time should not exceed 5 minutes for the OGM samples. Moreover, it is expected that the results calculated for the TGM-3 molecule can sufficiently describe its solid mixtures properties (e.g., the optical polarizabilities) as well.

II. Molecular structure

A main problem in understanding photochemical processes consists in revealing a mechanism that leads to a photopolymerization. In our opinion, one should consider a proper structure of the OGM components, particularly the TGM-3. The geometry optimization of the TGM-3 molecule was obtained in two steps. The first one was performed using standard methods of the molecular dynamics with a force field MM+ in a version represented by the HYPERCHEM 4.0 computer package.

The second step consisted in application of the unrestricted Hartree-Fock method (UHF) in a version of the MOPAC 6.0 package [5] with the PM3 parametrization [6]. The geometry was succesfully optimised by a derivative procedure presented in the MOPAC program using a Broyden-Fletcher-Goldfarb-Shanno method (BFGS) [8,9,10,11]. The iteration procedure was continued until energy and charge density convergence became smaller than 10^{-8}. We have used the BFGS method in order to minimise the system energy using a procedure of energy gradients decreasing to 10^{-8}. Correlation effects were also included by a proper choice of adjustable parameters since we have applied semiempirical methods for the geometry optimization. Calculated vector position components of the optimised atomic positions are presented in Table 1 for all atoms of the TGM-3 molecule.

The calculated molecular structure of the TGM-3 is also depicted in more visuable form in Fig.1. Oxygen, carbon and hydrogen atoms are denoted by big black, big grey and small empty circles, respectively. It is clearly seen that the spatial structure of this molecule is very built-up in space. The TGM-3 molecular structure is, on the other hand, very similar to structures of many biological systems. The central chain is non-linear and has a zigzag shape. C=O double chemical bonds are roughly „perpendicular" to the bend central chain in contrast to the double C=C bonds which are „collinear" although these two notions can not be exactly applied in the case of the non-linear chain.

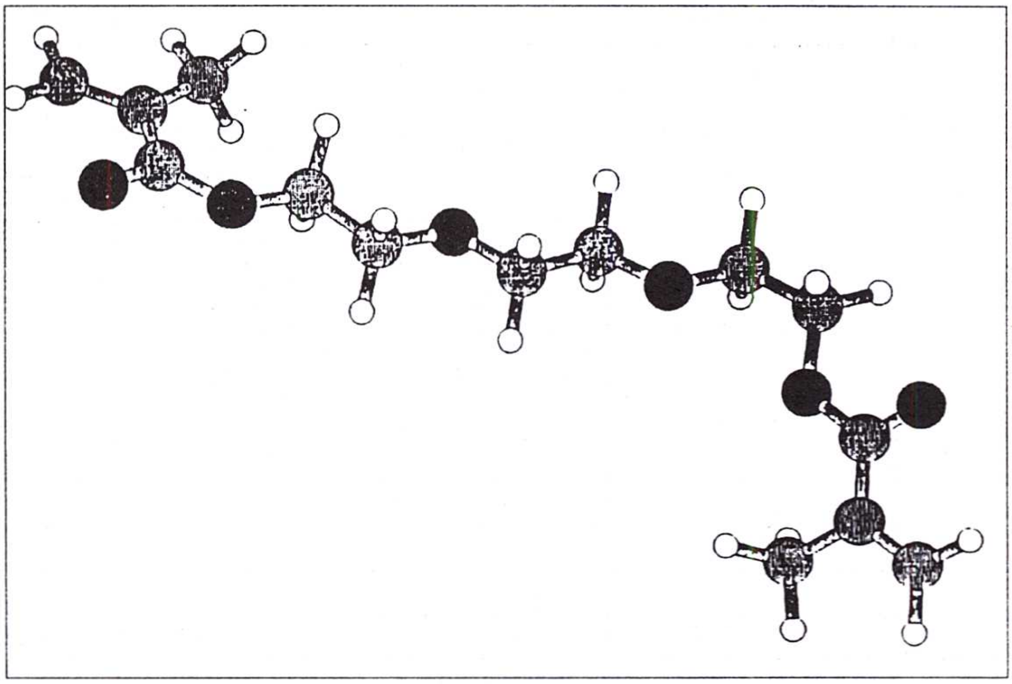


Fig. 1. Non-linear TGM-3 structure obtained after the geometry optimization using the HYPERCHEM 4.0 computer package. Oxygen, carbon and hydrogen atoms are denoted by big black, big grey and small empty circles, respectively

The presented molecular structure should ensure good elastic properties of the solid photopolymers because of its non-linearity and the presence of different chemical bonds. We therefore expect that an admixture of the TGM-3 polymer in different composition should enhance their mechanical properties and allow new possible scientific as well as industry applications.

Table 1.
Atomic number Z (dimensionless), effective atom charge Q (in elementary charge unit) and optimised atom position coordinates x, y, and z (in angstrom) for different atoms of the TGM-3 molecule

Atom	Z	Q	x	y	z
2	6	-0.101436	15.16370010	4.21008205	0.79063612
4	6	-0.019434	13.84617043	3.98631811	0.84869510
5	6	-0.177172	12.88671970	4.95184088	0.25369820
13	8	-0.250737	14.06513023	1.93526101	2.09274602
14	6	0.294996	13.36155033	2.75128007	1.52598202
15	8	-0.260531	12.08150005	2.29236507	1.64591503
16	6	0.023628	10.97842979	3.00538206	1.10810101
17	6	0.020638	9.74376678	2.15042400	1.42293799
20	8	-0.263990	8.63118362	2.84893489	0.88222349

21	6	0.020581	7.41467905	2.13047504	1.03451705
23	6	0.020478	6.31382990	3.01002908	0.42585611
25	8	-0.260184	5.13654089	2.21673012	0.44575131
26	8	-0.275524	0.81683761	0.35280150	0.70229667
29	6	0.021019	3.97760201	2.92536211	0.03812625
30	6	0.027566	2.81390905	1.92768896	0.02487470
31	8	-0.274706	2.36307406	1.80197299	1.37327504
32	6	0.310297	1.34303105	0.93342102	1.63468003
33	6	-0.008280	0.99176991	0.81622380	3.07778406
34	6	-0.108369	-0.04898083	0.06255176	3.44361901
36	6	-0.175029	1.82535601	1.54106700	4.07270098
10	1	0.058385	7.48379087	1.15210497	0.51907712
22	1	0.056783	7.22109699	1.92870200	2.10624695
11	1	0.059997	9.82655430	1.14250505	0.97009569
24	1	0.055365	6.17178917	3.94106293	1.00863004
12	1	0.061067	11.11575031	3.15809393	0.01514136
1	1	0.082827	15.90301991	3.53257298	1.21283996
27	1	0.077596	3.11629891	0.93898422	-0.37175629
28	1	0.052210	4.12288713	3.33784389	-0.97981572
3	1	0.070038	15.58403969	5.09258795	0.31434709
6	1	0.067947	12.30488968	4.47256804	-0.55225182
7	1	0.069356	13.38877964	5.83183193	-0.16718049
8	1	0.067690	12.16261959	5.30026913	1.00958395
18	1	0.060845	10.92051983	4.01533699	1.56961000
19	1	0.059493	9.61270237	2.01552701	2.51456189
35	1	0.077686	-0.66883701	-0.47952610	2.73338509
9	1	0.055580	6.55048323	3.30382895	-0.61553597
37	1	0.072489	2.87082291	1.20699596	4.02565193
38	1	0.071400	1.81399500	2.62315011	3.88386989
39	1	0.064358	1.47082305	1.38022602	5.09970522
40	1	0.067857	-0.34187841	-0.05878915	4.48332977
41	1	0.065855	1.99041295	2.31172800	-0.60659021
42	1	0.061365	3.79050708	3.77837491	0.72038919

III. Charge density distribution

Calculations of total charge density distribution were performed for deeper analysis of physical properties, first of all, of nature of the photoinduced changes. We have found a substantial charge density in a geometrical centre of the TGM-3 molecule. On other hand, the molecule backbones contribute to the charge density distribution to substantially smaller extent. The situation is clearly shown in Fig. 2 where total charges associated with a given atom are denoted. The total charges Q are also collected in column 3 in Table 1. It is easily seen that a typical backbone charge is one order in magnitude smaller than a spine site charge with obvious exception for the C=O double chemical bonds.

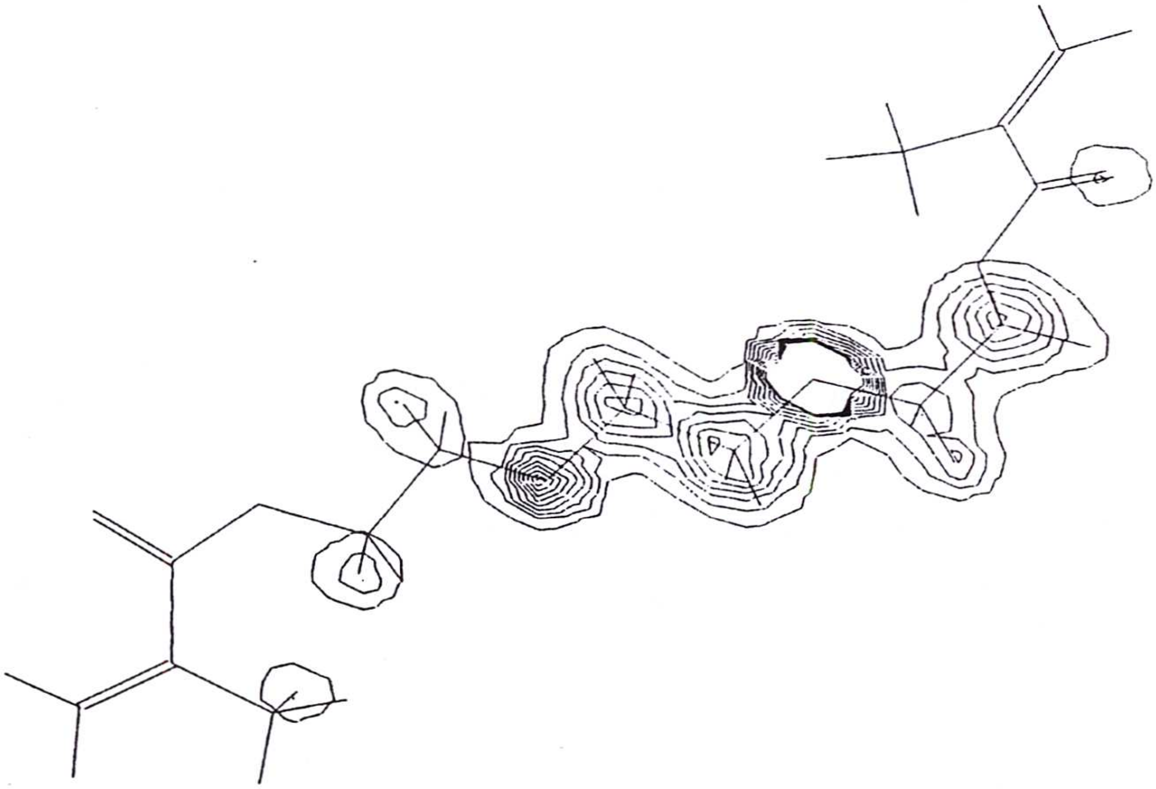


Fig. 2. Total charge density distribution of the TGM-3 molecule. A maximum charge density is observed in a central part of the molecule in contrast to the chain ends

The charge density distribution give us even a more informative opportunity to predict main susceptibilities of the system. The TGM-3 molecule will contribute only a bit to the hyperpolarizabilities as it is expected on the ground of the above presented charge distribution.

Electrostatic potentials are depicted in Fig. 3 to complete theoretical description of the system under investigation. A strict correlation between the charge density and the electrostatic potential distributions is clearly seen in close consistency with the standard electrostatic rules. Therefore, we will present only the charge density distribution (or its gradient) in future.

The TGM-3 compound is a chain-like polymer with acrylate backbones. The unique features of the TGM-3 system originate from its quasi-one-dimensional structure formed by σ-conjugations in the main chain and they are very sensitive to a distance between the C=O backbone groups.

Data obtained in [4] show an essential role of chain-like vibrations in formation of the temperature metastable noncentrosymmetric structural components in the solid polymers since optical experiments performed on relative olygomers (i.e., with no acrylate acids) have shown absence of any essential optical changes with decreasing temperature. Therefore, one can expect that these bonds just cause the low-temperature structural ordering. However, a nature of the observed phenomena is not yet clear in full and additional experimental as well as theoretical investigations should be performed to obtain a clear picture of the situation.

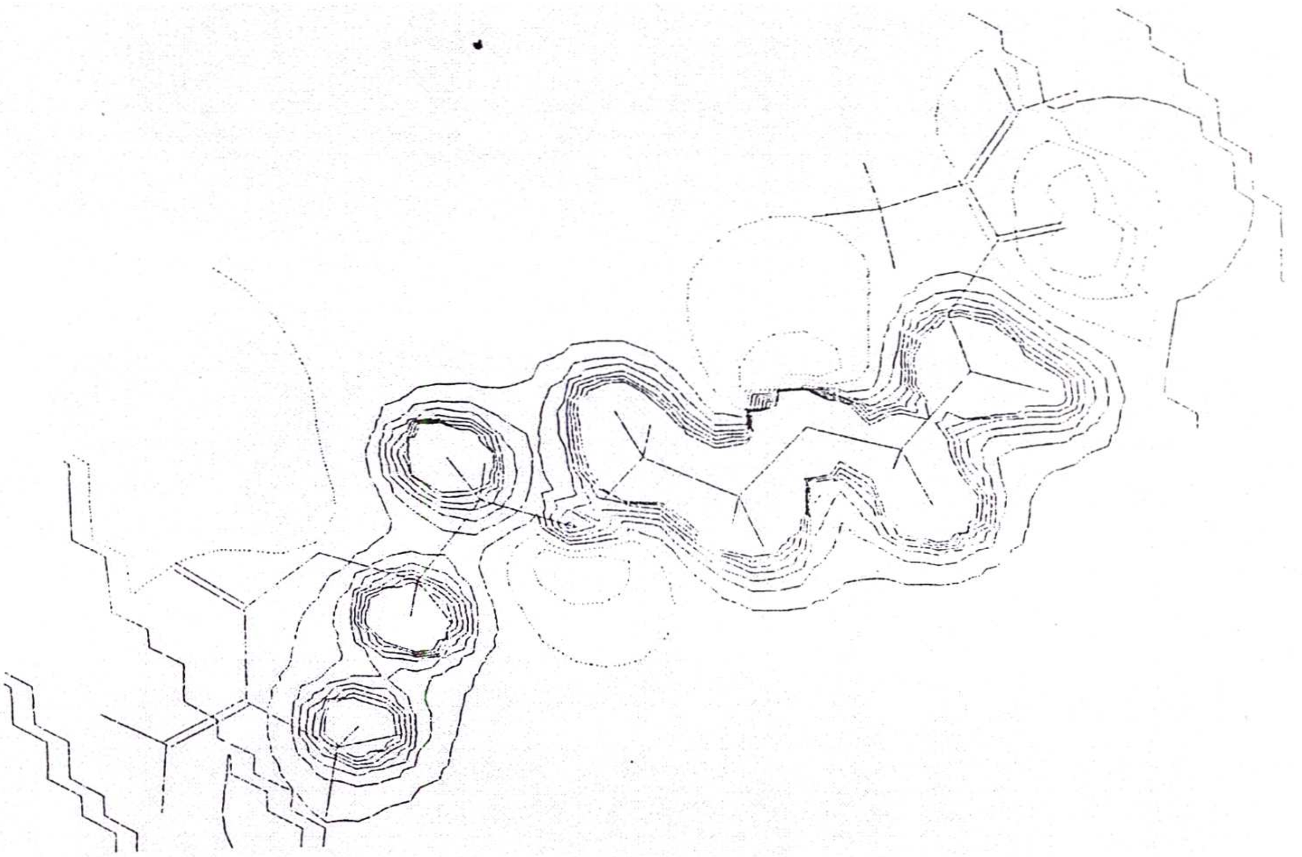


Fig. 3. Electric field potential obtained after the geometry optimization

It has been revealed in [4] that the acoustooptical susceptibilities are smaller for higher distances between the C=O groups. Therefore, the C=O chemical bonds lead to an increase of total polarizability of the methylene chains and appropriate weakening of the corresponding chemical bonds. In the result, we observe occurrence of the acoustooptical intensity which is caused by the local structural noncentrosymmetry in the photopolymer solids.

The electric dipole moment of the TGM-3 has been decomposed in a point charge and a sp-hybridization contributions that is shown in Table 2. It is seen that the dominant part of the dipole moment is governed by the point charge contribution and the sp-hybridization play a smaller role. Higher miltipole moments were also calculated and they are presented in Table 3. A substantial quadrupole moment is predicted on the ground of our calculations and one can expect possible quadrupole interactions to be responsible for appearance of the structural noncentrosymmetry in the solid photopolymer that is, of course, very important for the optical properties.

Table 2.
Point charge and sp hybridization contributions as well as their sum of electric dipole moment x-, y- and z-vector components and total value (in Debye) for the TGM-3 molecule

	x	y	z	Total
Point charge	- 0.357	3.653	-0.156	3.674
sp hybridization	- 0.159	0.502	-0.305	0.609
Sum	- 0.516	4.155	-0.461	4.213

Table 3.
Multipole moment components (units in brackets) for the TGM-3 molecule

Multipole moment			
Net charge (elementary charge)	0.0000		
Dipole moment (debye)			
	X: -0.4857	Y: 3.3450	Z: -0.7177
Quadrupole moment (debye angstrom)			
	XX: -128.6949	YY: -93.9006	ZZ: -108.8580
	XY: 32.5998	XZ: -23.1495	YZ: -1.1250
Octapole moment (debye angstrom^2)			
	XXX: -2710.9674	YYY: -709.9753	ZZZ: -428.0140
	XYY: -605.7992	XXY: 149.5941	XXZ: -471.5400
	XZZ: -853.7107	YZZ: -262.3374	YYZ: -145.1846
	XYZ: -10.2060		
Hexadecapole moment (debye angstrom^3)			
	XXXX: -56543.1018	YYYY: -4593.7529	ZZZZ: -2133.4829
	XXXY: -1655.5145	XXXZ: -7125.3392	YYYX: -6409.0461
	YYYZ: -734.3448	ZZZX: -2641.9206	ZZZY: -760.8446
	XXYY: -6910.5716	XXZZ: -9877.8049	YYZZ: -1189.8428
	XXYZ: -417.5817	YYXZ: -773.1036	ZZXY: -2485.3854

IV. One-electron energies

A semiempirical NDDO approach [11] with a PM3 parametrization [12] was applied in order to obtain useful informations concerning the electronic structure, the charge distribution and the optimised geometry of the TGM-3 molecule. It has been shown that the NDDO method (originally proposed by Pople) yields qualitatively better results than other methods. The NDDO approximation neglects differential overlaps in the case of the atomic orbitals of different atoms only, i.e., all one-center charge distributions are actually retained. The valence shell molecular orbitals are simultaneously represented by linear combinations of functions belonging to a minimum basis set of the valence shell atomic orbitals. The NDDO is especially reasonable method to describe ground states as it is widely known.

One-center terms appearing within the NDDO approach can be treated similarly and fitted to the corresponding spectroscopic values. Two-center two-electron repulsion integrals are usually given as a sum over semiempirical multipole-multipole interactions. The core-electron attraction and the core-core repulsion are expressed in term of the two-center repulsion integrals within such a semiempirical method. Calculated total energies of different nature are collected in Table 4 and can be in part subject to an experimental verification.

Table 4 .
Different energies calculated for the TGM-3 molecule

Quantity	Value
Total Energy	-614617.2037409 (kcal/mol)
Total Energy	-979.454738492 (a.u.)
Electronic Kinetic Energy	609070.1722235 (kcal/mol)
Electronic Kinetic Energy	970.614982183 (a.u.)
The Virial (-V/T)	2.0091
e-e and e-N Interaction Energy	-1519748.4740993 (kcal/mol)
Nuclear Repulsion Energy	905131.2703583 (kcal/mol)

The values of the binding energy indicate that the photopolymer can be solidified by a light from nearly visible spectral range. The latter can result in a chaotic polymerization that is difficult to be controlled and may influence measurements results as will be shown below.

On the other hand, we have also calculated one-electron energy eigenvalues which are presented in Table 5. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) contours are shown in Fig.4a and Fig.4b, respectively. It is seen that the contours differ significantly. One-electron energies of the HOMO and the LUMO are equal to - 8.187712 eV and 6.309898 eV, respectively. It is clearly seen that the theoretically predicted HOMO-LUMO energy gap of 14.497610 eV is very large and should influence the photopolymer properties.

Necessary measurements of light absorption by the liquid TGM-3 photopolymer were also performed in order to check our numerical calculations. Results obtained for the so-called fundamental edge for the liquid polymer are presented in Fig.5. One can extrapolate a value of minimum photon energy to be absorbed by the TGM-3 photopolymer material. This experimental gap value is equal to about 4.9 eV and is substantially smaller than the theoretical HOMO-LUMO energy gap for the TGM-3 single molecule.

Table 5.
Energy eigenvalues (in eV) of one-electron molecular orbitals for the TGM-3 molecule . The HOMO and LUMO energies are aditionally indicated by bold numbers

29.140854	29.614809			
21.820463	25.181301	25.312769	25.627419	26.908575
20.914293	21.341814	21.384912	21.488977	21.570360
19.635824	20.036867	20.163980	20.214106	20.701225
18.872475	19.001028	19.053921	19.232491	19.493631
18.333019	18.396938	18.618502	18.698664	18.759857
17.102898	17.306997	17.642864	17.733292	17.843845
15.997365	16.190723	16.408817	16.606615	16.768087
10.904883	12.882995	13.892195	14.396923	15.110849
		LU 6.309898	6.453609	10.653177
-8.243013	**HO - 8.187712**			
-9.230554	-9.209928	-9.154478	-8.974851	-8.958148
-11.155671	-11.009146	-10.769350	-10.560599	-9.302839
-12.990840	-12.975013	-12.792636	-12.711525	-11.888528
-14.402638	-14.127603	-13.841607	-13.540100	-13.442865
-15.129809	-14.997193	-14.827340	-14.675113	-14.540008
-16.072515	-15.950827	-15.775380	-15.645529	-15.426596
-17.763193	-17.315941	-17.178717	-17.075825	-16.973774
-21.780964	-21.563896	-20.892864	-18.606771	-18.484413
-24.880272	-24.681711	-24.398767	-22.437838	-21.958912
-34.372681	-28.708920	-28.466351	-27.198122	-26.276123
-37.509670	-37.420509	-35.837257	-35.509060	-34.441296
-301.012726	-300.750763	-300.710236	-300.557556	-300.308716
-302.197723	-302.122833	-302.065460	-302.045563	-301.049286
-550.783081	-303.786774	-303.726013	-302.359314	-302.338898
-552.126648	-551.995789	-551.448608	-551.425903	-550.795044

Origin of such a great difference should be explained. Of course, a natural broadening of the energy levels due to intermolecular interactions and to quasi-phonon vibrations is usually taken into account but such an effect can not be so large to cover the whole difference between the theoretical and experimental values. We therefore suggest that an actual reason of the discrepancy observed lies in fact that chemical reactions leading to a partial pre-polymerization in the liquid TGM-3 system and possible occurrence of larger molecules composed of many TGM-3 chains. Besides an experimental verification of the above assumption, there exist theoretical way to check it by performing proper calculations for the „multiplied" molecules. The calculations are now in progress although the computer time needed for this purpose is much longer than in the case of the single TGM-3 chain.

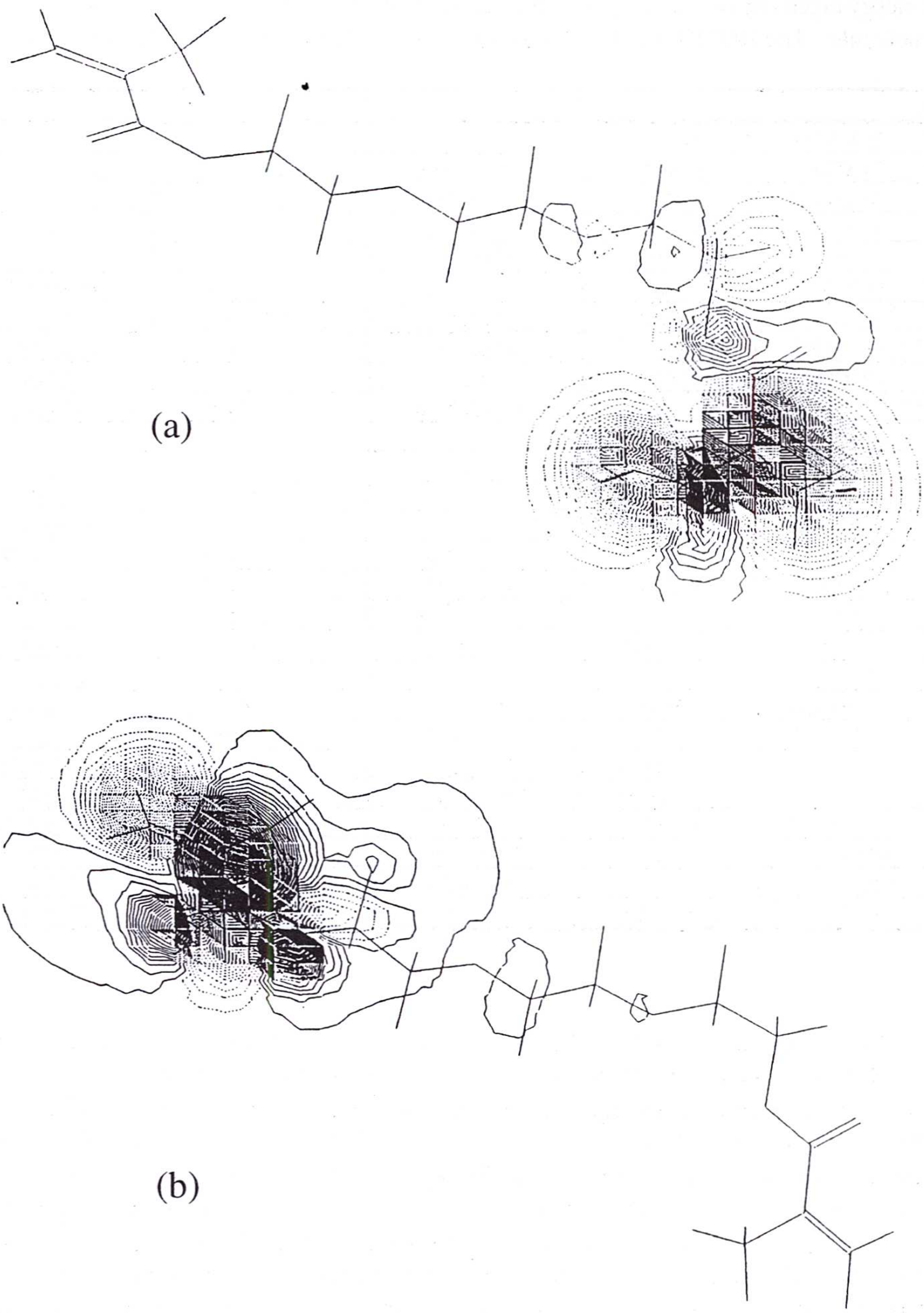


Fig. 4. HOMO (a) and LUMO (b) contours showing different spatial behaviours

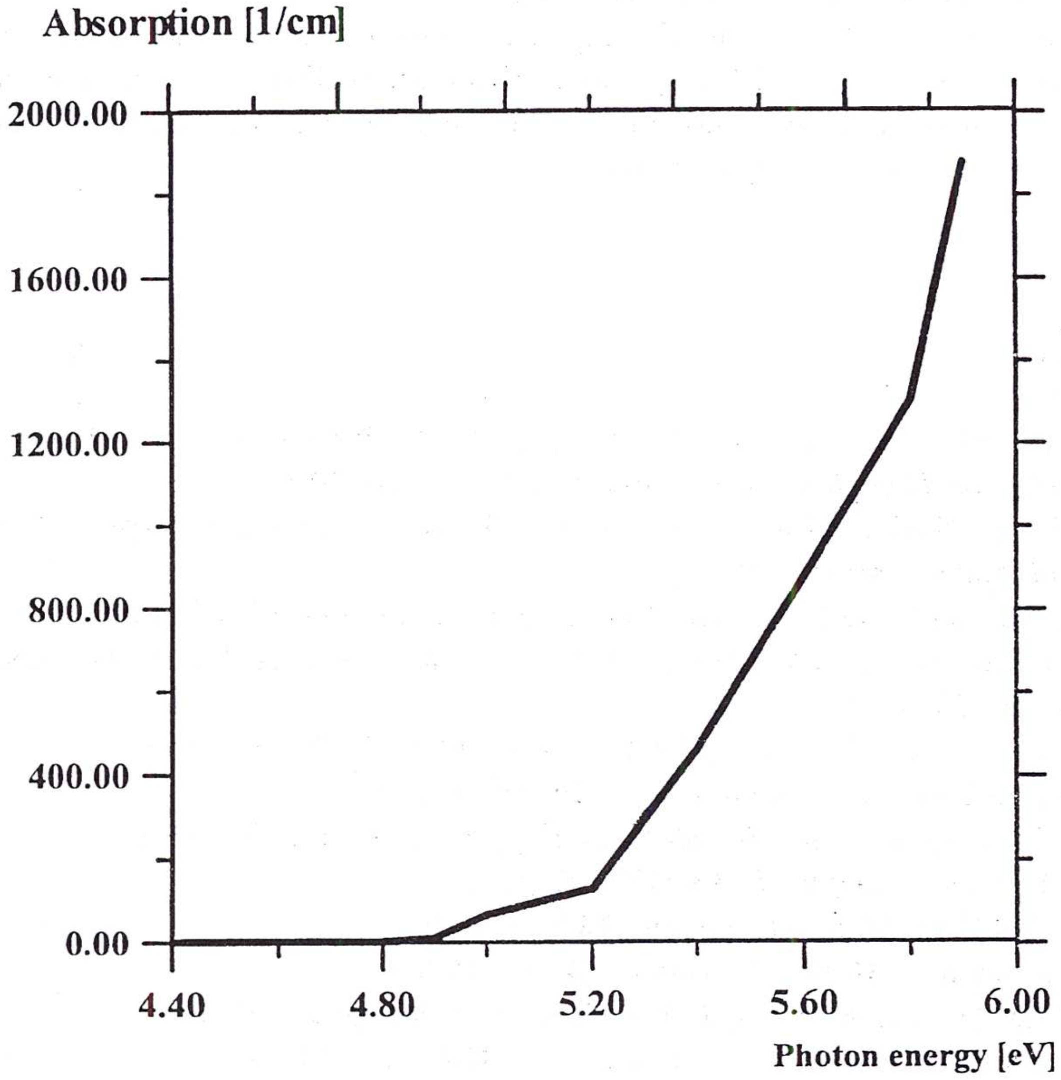


Fig. 5. Light absorption fundamental edge (in arbitrary units) as a function of photon energy (in eV). Energy gap of about 4.9 eV can be extrapolated from the curve

V. Conclusions

In the case of TGM-3 we have found a great charge density in the geometrical centre of the molecule. Therefore, this molecule weakly contributes to the hyperpolarizabilities of the polymer mixtures with its admixture.

Our semiempirical numerical investigations have shown the existence of the substantial energy gap determined by the HOMO-LUMO split. This value should determine an upper limit for the energy intervals between the highest occupied and lowest unoccupied electronic states in the solid system. One could conclude that the theoretical data obtained (for molecule) would not in formal agreement with the corresponding spectroscopic data. However, the pre-polymerization effect together with the natural broadening due to the intermolecular interactions and to the quasi-phonon vibrations should explain the discrepancy observed.

The data obtained for the OGM components indicate that the mechanic stability is mainly determined by the TGM-3 photopolymers due to their structure and chemical bonding. We therefore suggest possible use of the TGM-3 based materials to different research as well as practical applications.

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Structure and Optical Propertiesof TGM-3 Photopolymer

Summary

Molecular properties of the TGM-3 photopolymer have been investigated using a HYPERCHEM 4.0 computer package . Geometry of this photopolymer was successfully optimised and the obtained TGM-3 structure shows a very complicated non-linear shape. A total charge density of the TGM-3 is strongly nonuniform . C=O double chemical bonds are roughly perpendicular to a bended central chain. We have calculated a value of HOMO-LUMO energy gap which is not in agreement with our experimental data for fundamental absorption