
L-TYROSINE BASED CHIRAL POLY (ESTER-AMIDE) S CONTAINING AZO GROUP IN THE SIDE CHAIN

6.1. Introduction

Recently, a large number of azobenzene containing side chain and main chain NLO polymers ¹⁻⁵ have been reported. In the case of NLO materials that have to be poled before measuring NLO activity, prevention of relaxation of orientational order is the important goal to be achieved to make polymers useful for applications. Many approaches, for example guest-host system ⁶⁻⁸ and functionalized systems, ⁹ have been introduced for this purpose. Functionalized systems are classified into two; (i) side chain polymers (ii) main chain polymers. Side chain polymers have the chromophores as pendent side groups, with one end of the chromophore attached to the backbone. With main chain NLO active polymers, the chromophores are incorporated into the main chain. Poled order-relaxation may be restricted for chromophores, incorporated into the polymer backbone. The significant difference between this main chain and the side chain ones is that large, segmental motions of the polymer backbone are required for poling and relaxation of the former. The *cis-trans* isomerization of azo group is playing a major role in this orientational ordering. ¹⁰

In a chiral medium, external poling is not necessary, since chemical poling is achieved through the incorporation of chiral molecules or by chiral framework. But in chemical poling, polar ordering of the molecule is quite important so as to achieve high NLO response. In order to reduce the dipolar interaction and increase polar ordering in polymer materials the possibility of introducing main chain and side chain chromophores are to be explored. Very few efforts have been seen in the literature to study the side chain and main chain effects in chiral polymers. The chiral methacrylate polymers bearing side chain azobenzene chromophores has shown dipole-dipole interaction between the side chain azoaromatic chromophores, occurring as a

consequence of their anchorage to the polymer backbone, which favors their aggregation.¹¹

This chapter discusses the effect of side chain azo group in the chiral framework of L-tyrosine. The comparison is made with the polymers containing both the main chain and side chain azo group incorporated within the same L-tyrosine chiral framework. Poly (ester-amide) s with only side chain azo group has been designed and the properties were studied theoretically using *ab initio* and semiempirical methods. Subsequently, the systems were synthesized in the laboratory and SHG efficiencies were measured experimentally using Kurtz and Perry powder method.

6.2. Computational methods

6.2.1. Monomers

Because of the high computational demand in optimizing L-tyrosine based chromophores containing more than 400 electrons, all the monomers have been optimized using restricted Hartree-Fock (RHF) method with 6-31G basis sets available with the Gaussian 03 code. To avoid the geometry effects in the prediction because of high sensitivity of polarizability to geometry, all the geometries were optimized at the same level of theory.¹²⁻¹⁵ The SCF MO energies were computed at these optimized geometries. The *static* spectroscopic properties of monomers have been calculated using Coupled Perturbed Hartree-Fock (CPHF) method at RHF 6-31++G (d, p) level available in the Gaussian codes.¹⁶ The *dynamic* spectroscopic properties have been calculated using the Zerner's INDO-SOS method with sum over 82 states.¹⁷

6.2.2. Polymers

All the polymer geometries (three repeating units) have been optimized using the AM1 parameterized Hamiltonian available in the Gaussian 03 set of codes.¹⁸ For one of the polymer, the geometries obtained by AM1 calculations have been compared with geometries obtained using *ab initio* based methods using the 6-31G basis. Both the geometries have comparable bond lengths and bond angles. Geometry calculations are restricted to this semiempirical level neglecting the small changes in bond length and

bond angle so as to save high computational demand of *ab initio* method. Also, because of the very high cost of computation in calculating the properties of polymers (repeating units) using polarized and diffused basis sets, *static* molecular properties (CPHF) of polymers have been limited with 6-31 G (d) basis sets. The *dynamic* spectroscopic properties have been calculated using the Zerner's INDO-SOS method with sum over 82 states.

6.3. Designing of molecules

In this chapter, the main emphasis was on the chromophore design based on L-tyrosine. Since L-tyrosine is a potential chiral auxiliary for NLO active material, the goal has been pointed on the addition of nitroaromatics and donor-acceptor groups (e.g. *para*-nitroaniline, azo-acid chloride) into the L-tyrosine framework. The diols have been selected on the basis of the coupling ability with the L-tyrosine framework to form polymers with high β value. Both chiral and achiral diols have been selected so as to study the effect on the β value by the incorporation of chiral and achiral molecules in to a chiral medium.

6.3.1. Monomer design

6.3.1.1. Chromophore

The route of chromophore design is shown in Figure 6.1. Since the main aim of this chapter was to study the effect of side chain azo group in NLO response of chiral media, design of the system was done accordingly. The designing of the L-tyrosine chiral framework was explained in chapter 5. Up to (*S*)-2-amino-3-(3-(4-nitrophenylazo), 4-hydroxyphenyl) propanoic acid (PNATY, 3) the design followed the procedure of chapter 5. Then, instead of, azobenzene-4, 4'-dicarbonyl chloride (AZCI), the azo acid chloride, acylation of PNATY was performed with terephthaloyl chloride (TE, 4), a diacid chloride with out azo group. This acylation produced the chiral amide framework of (*S*)-2-terphthalamido- 3-(3-(4-nitrophenylazo)-4-hydroxyphenyl) propanoic acid (TYTE,5). Chlorination of TYTE yielded (*S*)-2-terphthalamido- 3-(3-(4-nitrophenylazo)-4-hydroxyphenyl) propanoic acid chloride (TYTECl, 6).

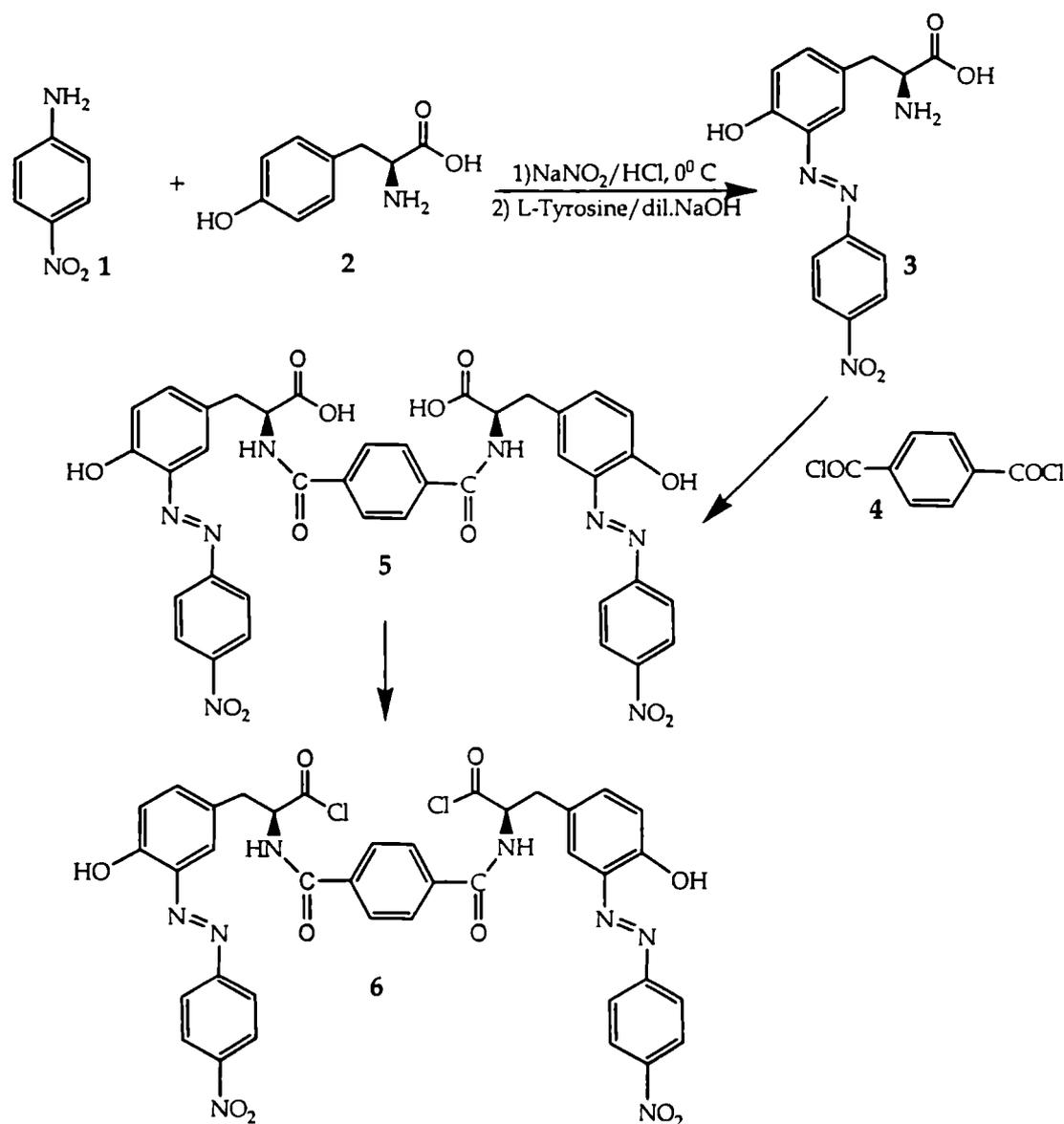


Figure 6.1. Route of chromophore design

6.3.1.1.1. Static and dynamic molecular property calculations

This chapter mainly deals with the comparison of properties of molecules containing side chain azo group with the molecules containing azo group in both the main chain and in the side chain. So, all the properties of this series of monomers and polymers were compared with the results obtained in chapter 5.

6.3.1.1.1. a. Comparison of dipole moment

The dipole moments of chromophores are summarized in **Table 6.1**. In both *static* and *dynamic* calculations, the azo acid chloride, AZCI has more dipole moment than the terephthaloyl chloride, TE, which was used as the diacid chloride with out the azo group in the design of chromophore containing azo group only in side the chain. Followed by TE, the chromophores designed from it, TYTE and TYTECI also have small dipole moments compared with TYAZ and TYAZCI.



Figure 6.2. Electron density in TYTECI

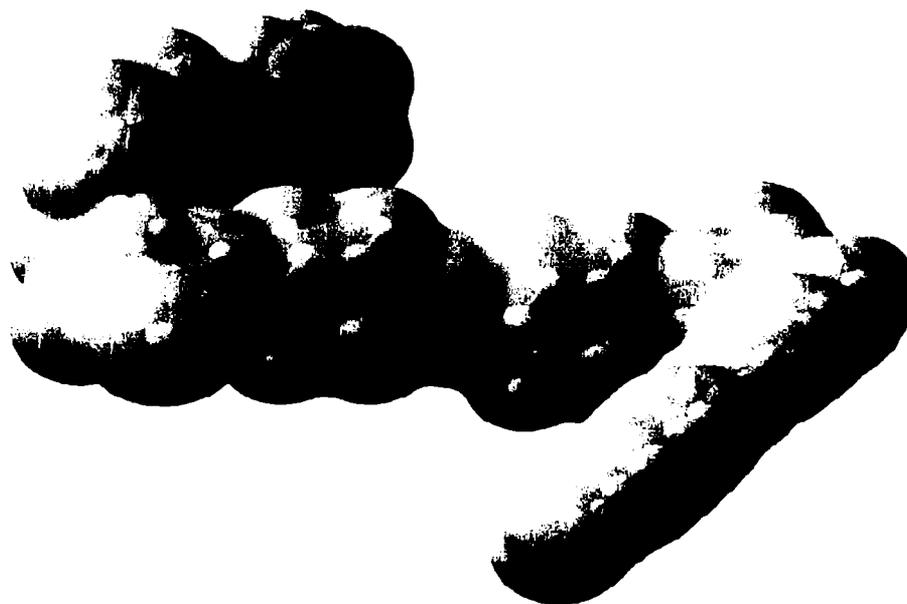


Figure 6.3. Electron density in TYAZCI

This can be attributed to the influence of two amide groups separated only by an aromatic ring. Amide groups are poor electron donors. But azo groups can act as both electron acceptor and electron donor. In the presence of -N=N- (azo) group, the electron density is more shifted towards the NO₂ group (one of the acceptors) and in the absence of azo group the shift of electron density towards the acceptors was reduced in TYTE and TYTECI. (Figure 6.2 and Figure 6.3)

Table 6.1: Comparison of dipole moments (in debye) of chromophores

Chromophore	μ_x	μ_y	μ_z	μ_g static	μ_g dynamic
PNA	6.9218	0.0026	-3.9362	7.9627	43.6312
Tyr	1.9130	1.5148	2.0806	3.2068	20.5722
PNATY	2.1497	1.5269	4.7942	5.4715	34.9174
AZCI	1.3614	0.0012	0.0114	1.3615	10.6268
TE	-1.1503	-0.0007	0.0006	1.1503	0.64485
TYAZ	7.6858	3.2330	-0.1818	8.3400	87.0284
TYTE	7.4275	0.1082	0.0000	7.4285	77.6828
TYAZCI	10.1682	4.5984	-0.0456	11.1598	99.5583
TYTECI	-0.0008	-0.0005	5.3988	5.3988	34.9915

6.3.1.1.1.b. Comparison of polarizability (α)

Table 6.2: Polarizability (α) of chromophores

Chromophore	α_{xx}	α_{yy}	α_{zz}	α (au)	$\alpha_{tot} \times 10^{-23}$ (Static*)	$\alpha_{tot} \times 10^{-23}$ (Dynamic*)
PNA	121.6103	48.7223	102.4463	90.9263	1.3474	411.0
Tyr	132.5928	81.8793	121.8485	112.1067	1.6613	294.0
PNATY	221.9997	122.9558	354.3746	233.1100	3.4544	866.0
AZCI	202.9226	102.1023	389.5218	231.5155	3.4307	927.0
TE	125.6097	61.8341	162.5198	116.6545	1.7287	416.0
TYAZ	545.6926	587.1834	812.9603	648.6121	9.6115	1350.0
TYTE	510.1612	572.2675	550.3932	544.2739	8.0654	1340.0
TYAZCI	505.0923	528.5364	701.7857	578.4714	8.5721	1430.0
TYTECI	521.96281	579.0277	561.6608	554.2171	8.2127	1310.0

* α (esu) = $0.148185 \times 10^{-24} \alpha$ (au)

The polarizability values of TE, TYTE and TYTECI were obtained from *static* method were found to be low when compared with AZCI, TYAZ and TYAZCI. The ZINDO *dynamic* values are also in agreement with *static* values. The polarizability values are summarized in Table 6.2.

6.3.1.1.1.c. Comparison of hyperpolarizability (β)

As in the case of the dipole moment (μ) and the polarizability (α), the hyperpolarizability (β) of TE, TYTE and TYTECI (the molecules without azo group in the main chain) is low as compared with AZCI, TYAZ, and TYAZCI (the molecules have an azo group in the main chain) respectively. This can be explained on the basis of HOMO-LUMO gap (ΔE). Table 6.3 gives the values of β and ΔE . The HOMO-LUMO gap of TE, TYTE and TYTECI is greater than AZCI, TYAZ, and TYAZCI. This helps for the easy charge transfer in the latter group of molecules compared to the former. Since the value of hyperpolarizability of organic molecules depends on the charge transfer from donor to acceptor part of the molecule, molecules with low HOMO-LUMO gap and thus facilitating easy charge transfer, have shown higher value of β .

Table 6.3: HOMO-LUMO gap (ΔE) in eV, Ground-State Dipole Moment (μ_g) in debye, Linear Polarizability (α) in units of 10^{-23} esu, and First Hyperpolarizability (β) in units of 10^{-30} esu for the chromophores (*ab initio* CPHF static property calculations)

Chromophore	ΔE	μ_g	α	β
PNA	0.3507	7.9627	1.3474	8.9445
Tyr	0.3461	3.2068	1.6613	1.3165
PNATY	0.3248	5.4715	3.4544	10.374
AZCI	0.3309	1.3615	3.4307	1.0072
TE	0.3883	1.1503	1.7287	1.0415
TYAZ	0.3264	8.3400	9.6115	8.0164
TYTE	0.3286	7.4285	8.0654	6.7954
TYAZCI	0.3320	11.1598	8.5721	11.2620
TYTECI	0.3284	5.3980	8.2127	5.1018

Dynamic property evaluation (ZINDO) gives exactly the same trend (Table 6.4) as static calculations. While examining TE and AZCI it can be seen that the oscillator strength, f of TE (0.3121 eV), which doesn't possess an azo group, is much lower than that of AZCI (1.3355 eV). Also, the optical gap, δE is higher in TE than in AZCI. Since easy charge transfer is determined by higher value of oscillator strength and lower value of optical gap, charge transfer is not as easy in TE as AZCI. Thus, although TE has higher value of $\Delta\mu$, the difference in dipole moment, its β value was very low compared to AZCI. In TYTE and TYTECI, the change in dipole moment, $\Delta\mu$ is very low compared to the change in dipole moment in TYAZ and TYAZCI. This lowers the value of β in the former compared to the latter azo molecules. It is notable that even the TYTE molecule containing the chiral building unit of tyrosine, its β value is lower than that of PNA (8.9445 esu) because of the low value of change in dipole moment, $\Delta\mu$ (2.5504 D).

Table 6.4: Oscillator strength f , Optical Gap (δE) in eV, Ground-State Dipole Moment (μ_g) in debye, Difference in dipole moments between ground state and excited state ($\Delta\mu$) in debye, Linear Polarizability (α) in units of 10^{-23} esu, and First Hyperpolarizability β , in units of 10^{-30} esu for the chromophores (ZINDO SOS dynamic property calculations)

Chromophore	f	δE	$\Delta\mu$	μ_g	α	β_{vec}
PNA	1.0285	7.4823	14.1337	43.6312	411.0	220.3553
Tyr	1.2761	7.6630	6.6922	20.5722	294.0	51.1458
PNATY	0.9677	4.0466	28.1308	34.9174	866.0	226.5886
AZCI	1.3355	4.1932	3.3658	10.6268	927.0	106.8586
TE	0.3121	5.2411	7.3867	0.64485	416.0	89.6450
TYAZ	2.6372	4.4560	19.9043	87.0284	135.0	655.9493
TYTE	2.6856	4.3285	2.5504	77.6828	1370.0	218.0021
TYAZCI	1.7055	4.4863	43.3013	99.5583	1430.0	740.2353
TYTECL	2.6094	4.3185	10.3396	34.9915	1310.0	367.7223

6.3.1.1.1.d. Comparison of chiral component

It is surprising that the amount of chirality is reduced by more than 50% in TYTE compared to TYAZ. This leads to the assumption that the azo group is playing an

important role not only in charge distribution but also in overall chirality. The *trans* form of the azo group imparts or translates the chirality through out the molecule.

Table 6.5: First hyperpolarizability of chromophores β (Static) in units of au

β Tensors	AZCI	TE	TYAZ	TYTE	TYAZCI	TYTECI
β_{xxx}	35.5150	-36.2513	-139.2570	-392.454	-315.5060	-200.889
β_{xxy}	0.0007	-0.01526	463.1576	9.18604	572.7625	9.4523
β_{xyy}	20.2807	-19.2325	-357.8430	-124.227	-390.9130	-114.725
β_{yyy}	0.0498	-0.02626	-575.2070	-4.2801	-816.2450	-3.9189
β_{xxz}	-1.9033	-0.00611	-368.2410	4.212456	-515.5590	4.3382
β_{xyz}	-0.0641	-0.0222	402.8543	-152.682	476.3268	-157.254
β_{yyz}	-0.0040	0.002373	350.8687	-4.19173	497.3552	-4.3606
β_{zzz}	60.3724	-65.0764	-395.2590	-269.903	-513.6710	-274.927
β_{yzz}	0.1063	-0.04249	-126.9660	-4.15401	-210.4860	-4.2415
β_{zzz}	-7.9310	-0.0247	104.5484	-0.33988	86.4357	-0.3386
β_x	116.168	-120.56	-892.3590	-786.583	-1220.09	-590.542
β_y	0.1568	-0.084	-239.0150	0.751927	-453.9680	1.2919
β_z	-9.8383	-0.02844	87.1761	-0.31915	68.2322	-0.3610
$\beta_{vec}(au)^*$	116.584	120.5603	927.9181	786.5838	1303.596	590.5437
$\beta_{vec}(esu)^*$	1.0100	1.0400	8.0200	6.800	11.3000	5.1018
%chirality	0.0549	0.0184	43.4148	19.4107	36.5394	26.6101

* β (10^{-32} esu) = 0.863916 β (au)

6.3.2. Polymer design

Design of polymers is based on the polycondensation of TYTECI with the previously designed chiral and achiral diols. Properties of diol molecules are explained in chapter 5. The repeating unit contains one TYTECI molecule and one diol molecule. All calculations have been performed for three repeating units. The structures of polymers are shown in Figure 6.4 and Figure 6.5 SHG efficiency has been compared with respect to 2-Methyl-4-nitroaniline (MNA) as the reference material. The structures

of MNA and polymers were optimized and properties were calculated using common level theory so as to avoid geometry effects in predictions.

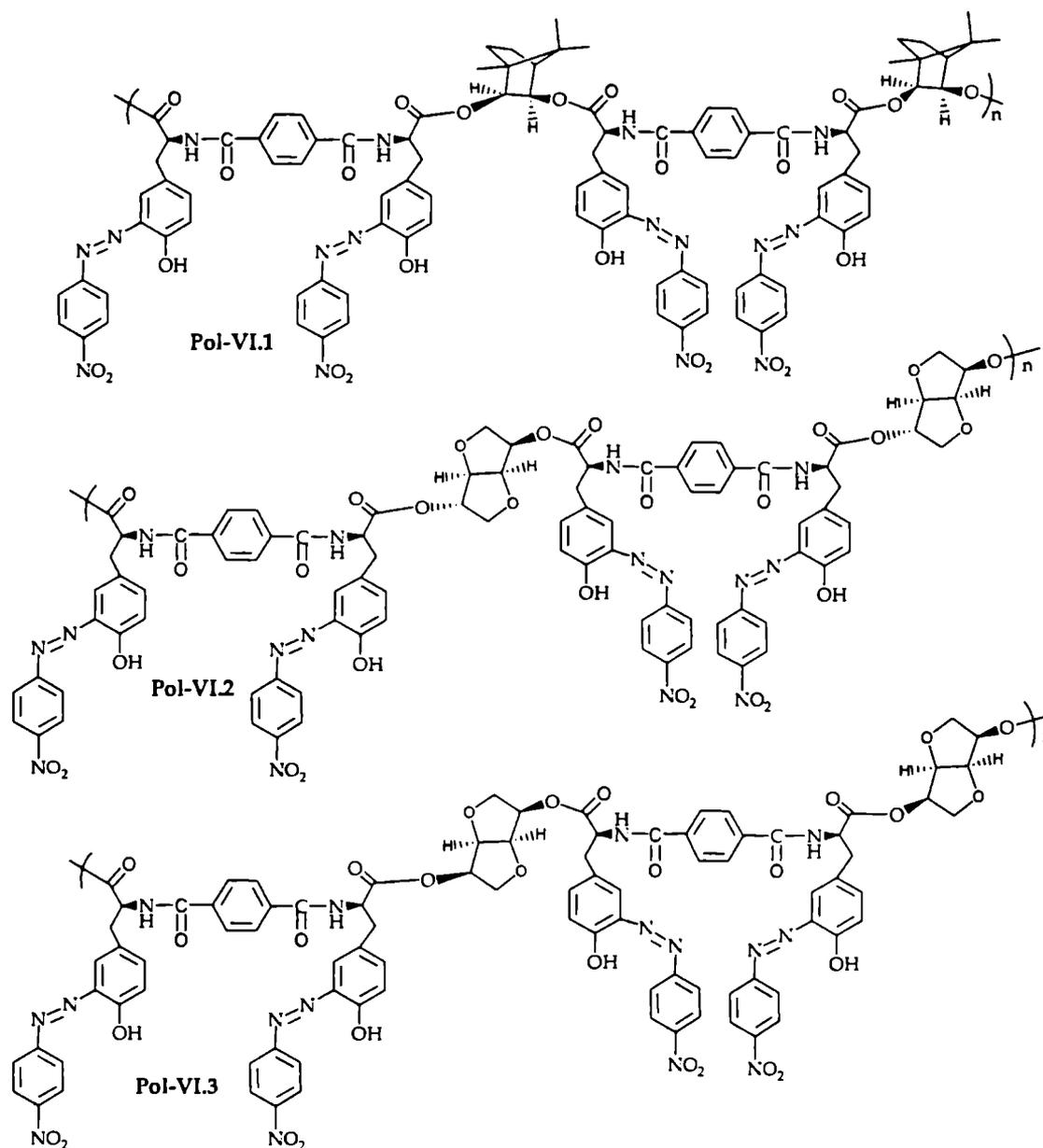


Figure 6.4. Structure of polymers (2 repeating units) incorporated with chiral diols (Pol-VI.1, Pol-VI.2, Pol-VI.3)

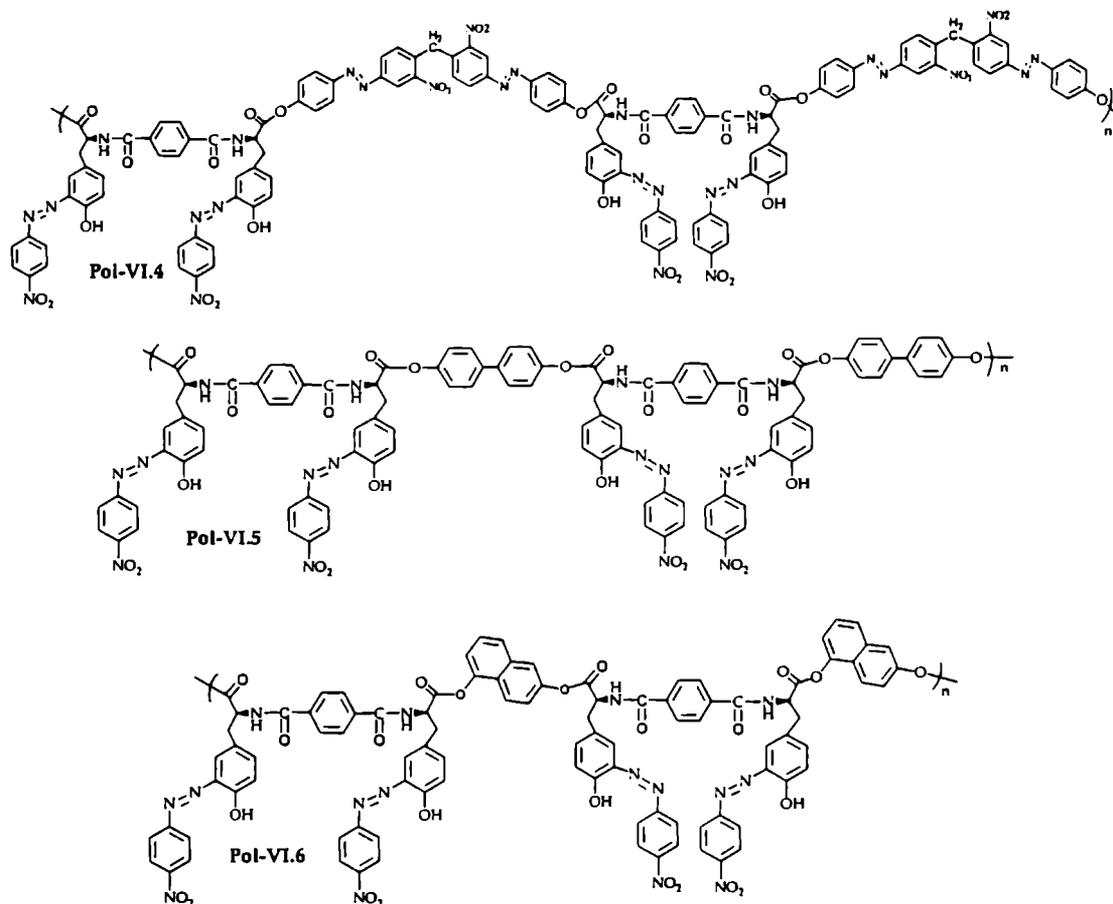


Figure 6.5. Structure of polymer (2 repeating units) incorporated with achiral diols (Pol-VI.4, Pol-VI.5, Pol-VI.6)

6.3.2.1 Static and dynamic molecular property calculations

The properties of the polymers without an azo group in the polymer main chain are compared with the properties of the polymers with an azo group in the polymer main chain. This will give the effect of azo group in determining spectroscopic properties. Even though the polymers with an azo group in the main chain contains an azo group in the side chain also, for convenience, they are named as main chain azo polymers and the polymers with azo group only in the side chain are named as side chain azo polymers. In Pol-VI.4, the achiral diol contains an azo group. Hence, in this polymer, the one repeating unit contains two azo groups whereas its analogue Pol-V.4 contains three azo groups in the main chain.

6.3.2.1.a. Comparison of dipole moment

As in the case of main chain azo polymers, the side chain azo polymers have also shown large dipole moment values compared to MNA. In *static* calculations, the side chain azo polymers incorporated with chiral diols have shown higher values of dipole moments compared to the dipole moments of main chain azo polymers incorporated with chiral diols. But surprisingly the side chain azo polymers with achiral diols have shown smaller values of dipole moment as compared with the main chain azo polymers incorporated with achiral diols. In dynamic calculations there is no such effect due to chiral and achiral diol. The dipole moment is lower in side chain azo polymers compared to main chain azo polymers. It is very much expected. The azo group is a good push-pull group than amide group. It imparts an effective electron push from donor to acceptor more easily than the amide group. The dipole moment values of polymers are summarized in Table 6.6.

Table 6.6: Dipole moment of polymers in units of debye

Polymers	μ_x	μ_y	μ_z	μ_s	μ_d
				Static	Dynamic
Pol-V.1	19.7620	8.7396	-0.8627	21.6255	242.1503
Pol-VI.1	22.6973	8.7306	-3.6824	24.5958	90.46477
Pol-V.2	38.5563	6.7376	0.4145	39.1428	572.2634
Pol-VI.2	33.4160	20.4653	9.5532	40.3326	283.7991
Pol-V.3	26.9111	6.0175	-1.2337	27.6033	286.6680
Pol-VI.3	31.1928	15.6559	16.9468	38.7980	282.1185
Pol-V.4	8.5608	25.3210	-15.6744	30.9859	423.9742
Pol-VI.4	14.9360	0.9432	-1.54860	15.0457	154.1610
Pol-V.5	34.1279	15.2220	-0.0963	37.3689	355.5187
Pol-VI.5	17.5007	0.1477	-0.0066	17.5014	166.0726
Pol-V.6	29.3493	13.4670	-0.2270	32.2923	332.3781
Pol-VI.6	15.8911	15.7878	22.9769	32.0893	284.8405
MNA	0.1357	1.3755	-6.8645	7.0023	40.0614

6.3.2.1.b. Polarizability (α)

Linear polarizability values are shown in Table 6.7. The chirality of the constituent diols didn't affect the polarizability values. All the side chain azo polymers have high α values with respect to MNA as in the case of main chain azo polymers. But from both *static* and *dynamic* calculations the α values of side chain azo polymers are smaller than that of main chain azo polymers. This indicates that the trends in the dipole moment as predicted from *dynamic* calculations have been followed in the prediction of polarizability values.

Table 6.7: Polarizability α of polymers

Polymers	α_{xx}	α_{yy}	α_{zz}	α (au)	$\alpha_{tot} \times 10^{-23}$	
					Static*	Dynamic*
Pol-V.1	2022.926	2224.921	2758.197	2335.3480	34.6060	4056.480
Pol-VI.1	2032.6692	2079.1745	2284.2422	2132.029	31.5936	3348.000
Pol-V.2	1752.230	2303.824	2468.601	2174.8854	32.2290	3091.680
Pol-VI.2	2190.6785	1512.4996	2051.7973	1918.325	28.4268	152.928
Pol-V.3	1759.414	2276.693	2437.519	2157.8752	31.9770	3340.800
Pol-VI.3	2002.3277	1730.1354	1939.0959	1890.52	28.0148	3216.960
Pol-V.4	2637.1810	2438.77	2499.221	2525.0572	37.4100	5732.950
Pol-VI.4	2527.8793	2480.4853	2250.0248	2419.463	35.8529	5677.920
Pol-V.5	1952.120	2572.932	3032.917	2519.3229	37.3330	3421.440
Pol-VI.5	2654.3335	1924.4479	2177.4319	2252.071	33.3724	3057.920
Pol-V.6	1809.624	2338.003	2943.665	2363.7641	35.0280	3304.800
Pol-VI.6	2151.1599	1751.8219	2549.4134	2150.798	31.8717	2728.800
MNA	99.4808	38.78715	122.8410	87.0363	1.2898	400.0012

* α (esu) = $0.148185 \times 10^{-24} \alpha$ (au)

6.4.2.1.c. Comparison of hyperpolarizability

Static (CPHF) hyperpolarizability values (Table 6.8.) of side chain azo polymers diverted from the dipole moment and polarizability trends. The values of β are higher for all the side chain azo polymers when compared to the main chain azo polymers,

while dipole moment, μ_g is higher only for chiral diol containing polymers and polarizability, α values are smaller in all side chain azo polymers irrespective of whether incorporated with chiral or achiral diol. The HOMO-LUMO gaps of side chain azo polymers are not adequate to explain this increase in β . In fact, the gap is higher in side chain azo polymers compared with the main chain azo polymers. This anomaly may be due to the inadequacy of *static* calculation (without much electron correlation)

Table 6.8: HOMO-LUMO Gap (ΔE) in eV, Ground-State Dipole Moment (μ_g) in debye, Linear Polarizability (α) in units of 10^{-23} esu, and First Hyperpolarizability, in units of 10^{-30} esu for the polymers (ab initio CPHF static property calculations)

Polymers	ΔE	μ_g	α	β_{vec}
Pol-V.1	0.3134	21.6255	34.6060	35.9861
Pol-VI.1	0.3398	24.5958	31.5936	66.3681
Pol-V.2	0.3343	39.1428	32.2290	14.4112
Pol-VI.2	0.3344	40.3326	28.4268	68.6399
Pol-V.3	0.3374	27.6033	31.9770	18.8488
Pol-VI.3	0.3366	38.7980	28.0148	87.4436
Pol-V.4	0.3243	30.9859	37.4100	26.9000
Pol-VI.4	0.3178	15.0457	52.1533	65.108
Pol-V.5	0.2925	37.3689	37.3330	33.6258
Pol-VI.5	0.3124	17.5014	33.3724	43.4443
Pol-V.6	0.2836	32.2923	35.0280	34.7583
Pol-VI.6	0.3080	34.1473	31.8717	30.0192
MNA	0.3970	7.0023	1.2898	5.2684

Results of *dynamic* ZINDO-SOS calculation are presented in Table 6.9. It is surprising that, in contrast to *static* calculations, the β values of all side chain azo polymers are lower than that of main chain azo polymers. This can easily be explained on the basis of two-level parameters, oscillator strength (f), optical gap (δE) in eV, and difference in dipole moments between ground state and excited state ($\Delta\mu$). In all the side chain azo polymers either f or $\Delta\mu$ is smaller than that of main chain azo polymers. These parameters decrease the value of β . In a chemical perspective, this can be explained on

Table 6.9: Oscillator strength (f), Optical Gap (δE) in eV, Ground-State Dipole Moment (μ_g) in debye, Difference in dipole moments between ground state and excited state ($\Delta\mu$), Linear Polarizability (α) in units of 10^{-23} esu, and First Hyperpolarizability in units of 10^{-30} esu for the polymers (ZINDO-SOS dynamic property calculations)

Polymer	F	δE	$\Delta\mu$	μ_g	α	β_{vec}
Pol-V.1	5.3562	13.4529	133.6228	242.1503	405.648	2168.197
Pol-VI.1	4.9411	15.0393	135.6050	90.4648	3348.00	1805.727
Pol-V.2	0.4684	17.7927	240.6799	572.2634	15.2928	762.805
Pol-VI.2	4.4928	15.4335	155.7673	283.7991	3091.68	737.973
Pol-V.3	5.0169	14.3649	142.4032	286.6680	334.080	1536.880
Pol-VI.3	4.1369	14.9172	111.1800	292.1185	3216.96	1120.704
Pol-V.4	3.9045	15.0972	168.9320	423.9742	400.9702	1797.502
Pol-VI.4	3.1214	13.6887	237.6463	154.1610	5677.92	1278.510
Pol-V.5	4.0649	13.8318	185.4564	355.5187	342.144	1966.639
Pol-VI.5	7.7026	17.0856	57.4468	166.0726	4057.92	1222.223
Pol-V.6	4.1477	14.0781	126.1178	332.3781	330.480	1466.959
Pol-VI.6	4.2878	15.7644	133.4538	284.8405	2728.80	1078.004
MNA	0.9502	8.2721	12.0416	39.5013	300.8571	182.464

the basis of difference in electron distribution in the presence and absence of azo group. Azo group is a good electron donor (and acceptor also), hence the total charge distribution is uniform through the polymer chain when an azo group is present in the main chain. While in the absence of azo group, this electron distribution breaks at amide group. This is because of the reason that the amide group is not a good donor and in most cases it acts as an acceptor. When an azo group is present in the main chain near to the amide group, it takes the electrons from the main chain azo group and forms weak donor-acceptor system with amide group. This leaves the side chain azo electrons for -NO₂ group. Thus side chain azo -NO₂ system acts as very good donor-acceptor system. Hence, in polymers with main chain azo group, two donor-acceptor systems compliment very well and give good SHG response. While in side chain azo polymers, there is no azo group in the main chain. So the acceptor amide group takes the electron from the side chain azo group and forms a weak donor-acceptor system. So there is a

competition between amide group and the side chain $-\text{NO}_2$ group for the same azo group electrons. This highly reduces the strength of azo $-\text{NO}_2$ donor acceptor system. Hence, in principle, side chain azo polymers occupied with two weak donor-acceptor systems have reduced the SHG response.

6.4.2.1.d Comparison of chiral component

Table 6.10: First hyperpolarizability tensors of Polymers β (Static) in atomic units

#	Pol-V.1	Pol-VI.1	Pol-V.2	Pol-VI.2	Pol-V.3	Pol-VI.3	Pol-V.4	Pol-VI.4	Pol-V.5	Pol-VI.5	Pol-V.6	Pol-VI.6	MNA
β_{xxx}	-1048.33	-3877.8	500.3188	-5353.2	219.2635	-3417.4	503.6268	2747.17	-997.694	-1164.5	-988.283	-2355.26	-24.4201
β_{sxy}	1677.457	579.748	921.6536	-3867.2	990.8157	-1515.3	274.3517	-319.55	1827.039	0.38799	1731.973	-1123.06	13.5831
β_{yyv}	-1200.67	-3243.1	-1551.85	-2781.0	-1841.85	-904.55	129.2712	-3880.2	-1282.98	-593.12	-1200.15	-867.425	12.7643
β_{yyy}	-2466.73	-3793.7	-399.395	-2186.7	-920.593	-3055.6	239.5554	390.385	-2552.55	-16.016	-2521.87	-449.051	7.1032
β_{xiz}	-1509.88	1497.74	-568.978	-1737.0	-611.594	-921.24	2856.3440	285.192	-1525.0	10.7791	-1474.58	-1218.14	-137.669
β_{syz}	2389.433	-1352.4	1191.205	-1190.6	1234.665	-983.50	983.1450	-381.27	1406.965	-652.02	1369.3	-986.331	0.9190
β_{yyz}	1454.972	-36.339	373.3215	-890.71	613.6915	-2362	-973.1370	231.146	1440.737	-10.681	1437.96	-2509.48	-26.7852
β_{szz}	-1627.78	-56.161	-561.931	199.202	-537.314	-217.83	-329.5080	779.452	-1380.15	-956.04	-1565.74	-1191.17	15.0008
β_{yzz}	-717.775	829.839	-109.928	120.494	-239.676	-1137.8	2485.348	-188.86	-577.409	-7.4176	-635.238	-1257.68	-20.2272
β_{zzz}	279.673	-111.56	98.7310	558.592	255.3821	132.547	-1103.590	138.677	308.7788	0.1054	286.566	-830.418	774.2734
β_x	-3876.78	-7177.0	-1613.46	-7935.0	-2159.9	-4539.8	303.3897	-353.55	-3660.82	-2713.6	-3754.17	-4413.86	3.3450
β_y	-1507.05	-2384.1	412.3308	-5933.4	-169.454	-5708.7	2999.255	-118.03	-1302.92	-23.046	-1425.14	-2829.8	0.4592
β_z	224.7625	1349.83	-96.9257	-2069.2	257.4799	-3150.7	779.6211	655.016	224.5186	0.2035	249.9474	-4558.04	609.8187
β_{vec}^a	4165.467	7682.24	1668.131	10121.8	2181.788	7945.20	3113.741	753.641	3892.251	2713.72	4023.337	6947.347	609.8281
β_{vec}^b	36.00	66.40	14.40	87.40	18.80	68.6	26.9001	6.51	33.60	23.40	34.8	30.00	5.27
\$	57.3629	17.6042	71.4095	11.7627	56.5895	12.3785	31.2534	50.5904	36.1478	27.0267	34.0339	14.1972	0.1506

= β Tensors * $\beta_{vec} \times 10^{-30}$, β (10^{-32} esu) = 0.863916β (au), \$ = %chirality a = β_{vec} in au b = β_{vec} in esu

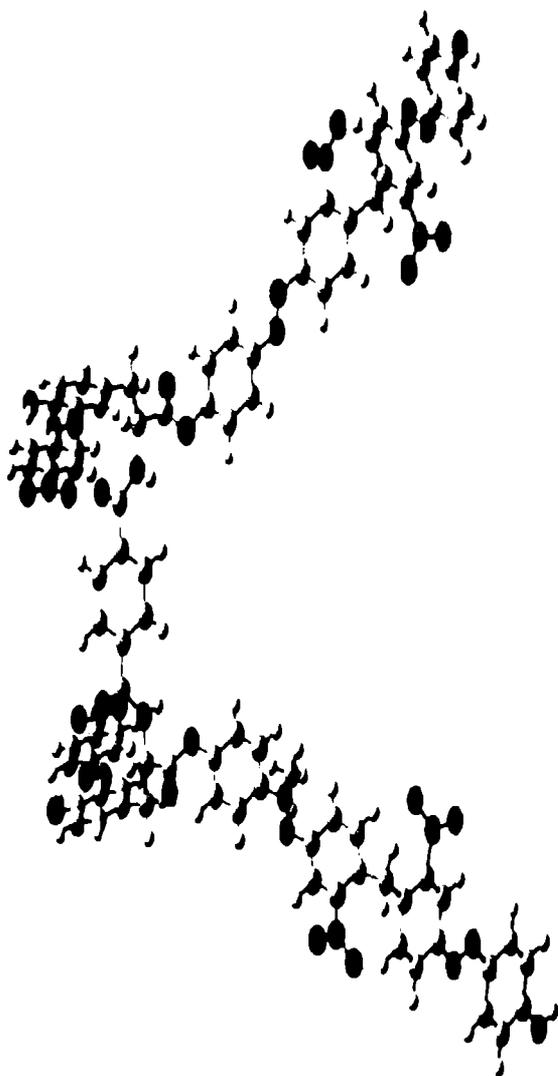


Figure 6.6. Optimized Structure of Pol-VI.4 (One repeating Unit)

polymers with main chain azo polymers, it can be seen that main chain azo polymers have more β_{xyz} values than side chain azo polymers. Due to the absence of azo group in the main chain the polymer chain lacks the helicity. This can be easily understood from the **Figure 6.6**. The presence of main chain azo groups (i.e. the azo group present in the chiral framework) imparts the helicity of the polymer main chain. This increases the overall chirality of the polymer chain and hence the β_{xyz} value. Even though **Pol-VI.4** contains one main chain azo group (from diol), it could not produce a helicity in the

In the first sight of **Table 6.10**, it was very surprising that the percentage chirality is small for chiral diol incorporated side chain azo polymers than that of the achiral diol incorporated side chain azo polymers. But when examining thoroughly, it can be seen that the β_{xyz} values of side chain azo polymers incorporated with chiral diols are larger than those incorporated with achiral ones. The percentage chirality is calculated as a percentage of total hyperpolarizability values, β . Since β is small in the chiral diol incorporated side chain azo polymers, the percentage chirality is also small. But the exact values of β_{xyz} are larger only in chiral diol incorporated side chain azo polymers than the achiral diol incorporated ones. Comparing the values of β_{xyz} of side chain azo

optimized structure. (Figure 6.6.) Hence, from the *dynamic* calculations and from the chiral parameter it can be concluded that the main chain azo polymers are better material for SHG.

6.4. Synthesis

For comparing the influence of incorporating azo group in the main chain and side chain effect of poly (ester-amide) s, a series of side chain azo polymers based on L-tyrosine framework has been designed and the spectroscopic properties were calculated using *static* and *dynamic* methods. *Dynamic* calculations revealed that the side chain azo polymers are poor SHG materials compared to the main chain azo polymers. To study the side chain and main chain effect experimentally, these polymers were synthesized and SHG efficiency was measured using Kurtz and Perry powder method. Six polymers were synthesized from L-tyrosine framework and diols (chiral and achiral) by high temperature polycondensation method. The following section deals with the synthetic procedures

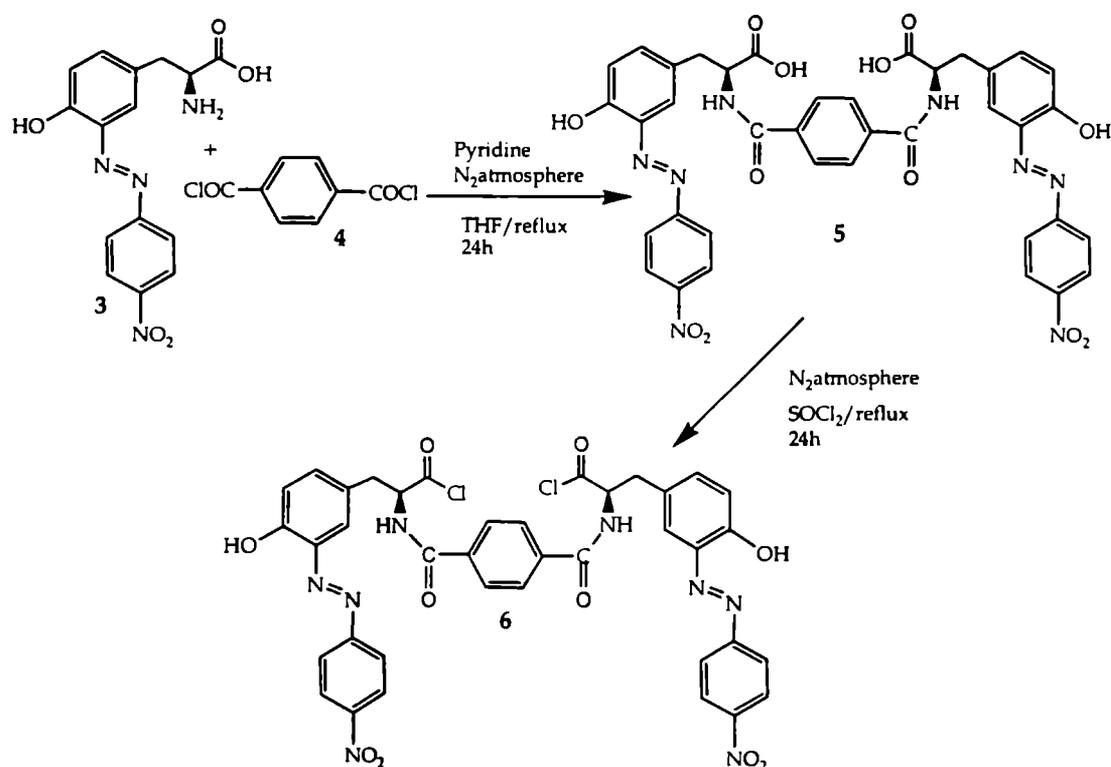
6.4.1 Monomer synthesis

6.4.1.1 Synthesis and characterization of chiral chromophore

L-Tyrosine based chiral chromophore was synthesized by a three-step process. In the first stage L-tyrosine was coupled with *para* nitroaniline to get PNATY. Synthesis of (S)-2-amino-3-(3-(4-nitrophenylazo)-4-hydroxyphenyl) propanoic acid (PNATY) was described in chapter 5. In the second stage, PNATY was acylated with terephthaloyl chloride to get TYTE. Chlorination of TYTE yielded TYTECl.

Synthesis of (S)-2-terephthalamido- 3-(3-(4-nitrophenylazo), 4-hydroxyphenyl) propanoic acid chloride (TYTECl, 6).

Terephthaloyl chloride (TE, 4) and (S)-2-amino-3-(3-(4-nitrophenylazo), 4-hydroxyphenyl) propanoic acid (PNATY, 3) were used for the synthesis of (S)-2-terephthalamido- 3-(3-(4-nitrophenylazo)-4-hydroxyphenyl) propanoic acid chloride (TYTECl, 6).



Scheme 6.1 Synthesis of TYTECI

PNATY (3) (1, g, .00316 mol) and terephthaloyl chloride, 4 (TE, 0.321g, 0.00158 mol) were added to a 50 mL three necked round bottom flask equipped with mechanical stirring and heating. THF (15 mL) was added as solvent. To this mixture, few drops of pyridine was added. The reaction was carried out for 24h at reflux temperature under nitrogen atmosphere. The reaction mixture was cooled and filtered. Dark brown solid of TYTE was obtained. This product was recrystallized from methanol (M.P 244^o C). The recrystallized product TYTE was refluxed with SOCl₂ for 24h under nitrogen atmosphere to obtain TYTECI (6). The reaction mixture was cooled, filtered and recrystallized from acetone.

Characterization

Yield 86%, $[\alpha]_D -11.3^{\circ}$ Decomposed at 209. 31^o C

Elemental analysis: Calculated for C₃₈H₂₈Cl₂N₈O₁₀ - C, 55.15; H, 3.41; N, 13.54. Found - C, 55.10; H, 3.42; N, 13.55

Spectral properties

UVλ_{max} nm: 300 (NO₂), 379 (-N=N-)

IR(KBr pellet) cm^{-1} : 3405 (NH⁺, NH st), 3073(-OH st), 1740(carbonyl of acid chloride), 1689 (carbonyl of amide), 1525 (NO₂ st as) 1438 (-N=N- st, 1332 (-NO₂ st ay) 1279 (aromatic trans -N=N-)

¹H NMR (300 MHz DMSO-d₆): δ 9.4 (2H, phenolic -OH), 8.61 (d, 4H aromatic, near to NO₂), 8.52 (4H aromatic, near to -N=N-), 8.21 (4H, aromatic hydrogen from acid chloride), 7.9 (d, 2H, amide hydrogen), 7.5 (d, 2H, amino acid phenyl ring near to -N=N-), 7.1 (d, 2H, amino acid phenyl ring near to -CH₂) 6.9 (d, 2H, amino acid phenyl ring near to -OH), 4.0 (m, 2H, -CH), 2.8, 2.5 (d, 4H, -CH₂)

¹³C NMR (75 MHz DMSO-d₆): δ 175.6 (-CO, acid chloride), 170.1 (-CO, amide), 161.1, 154.6, 152.6 140.4, 136.3, 132.4, 130.2, 127.8, 126.4, 125.1, 124.7, 118.1 (aromatic), 69.4 (4CH), 34 (-CH₂)

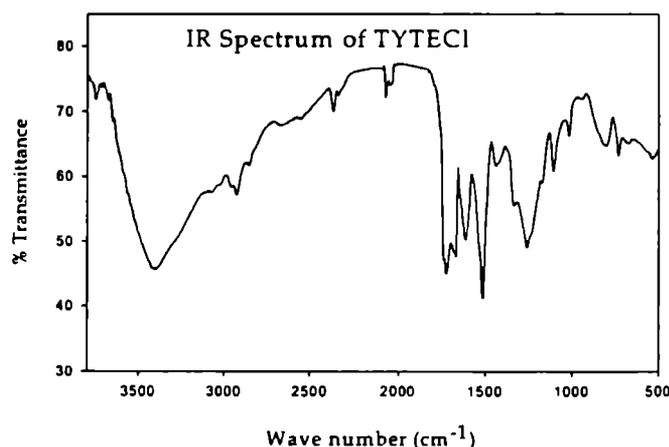


Figure 6.7. IR Spectrum of TYTECI

In the IR spectrum,(Figure 6.7) a structured band at 3405 cm^{-1} indicates the presence of (C=O)-Cl, hydrochloride of amino acids (confirmed chlorination of TYTE). Two distinct bands at 1740 cm^{-1} and 1689 cm^{-1} indicates two types of carbonyl functionality. The band at 1740 cm^{-1} is due to the carbonyl of acid chloride and the latter at

1689 cm^{-1} is due to the amide carbonyl. This confirmed the poly (ester amide) formation. The intensity of -N=N- str. band is less in TYTECI compared to TYAZCI which indicates the decrease in the concentration of azo group.

Six different types of hydrogens in the ¹H NMR spectrum (Figure 6.8) confirmed the disubstitution at terephthaloyl chloride. Monosubstitution would have given eight different hydrogens. Absence of off field peak confirmed the absence of carboxylic -OH hydrogen and thus confirmed chlorination. The peak due to -CH hydrogen was shifted to δ 4.0 which was due to the presence of -COCl near to -CH.

Twelve carbons in aromatic region of ^{13}C NMR spectrum (Figure 6.9) confirmed disubstitution at acid chloride. The peaks at δ 170.1 (due to amide $-\text{CO}$ group) and peak at δ 175.6 (due to carboxylic $-\text{CO}$) also indicated two different carbonyl groups which confirmed the proposed structure.

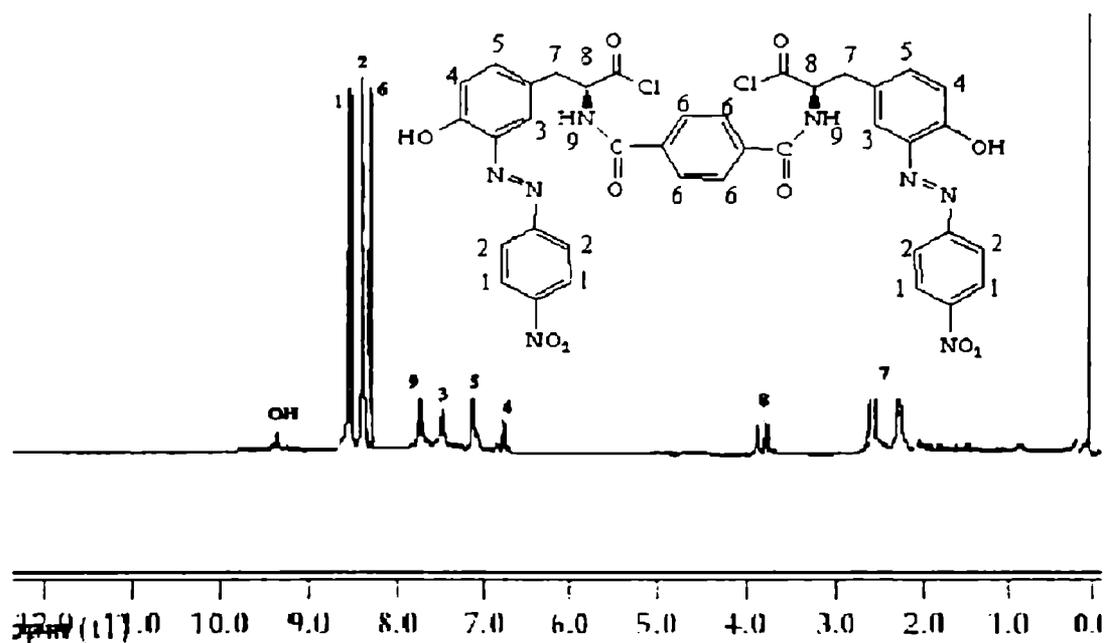


Figure 6.8. ^1H NMR spectrum of TYTECl

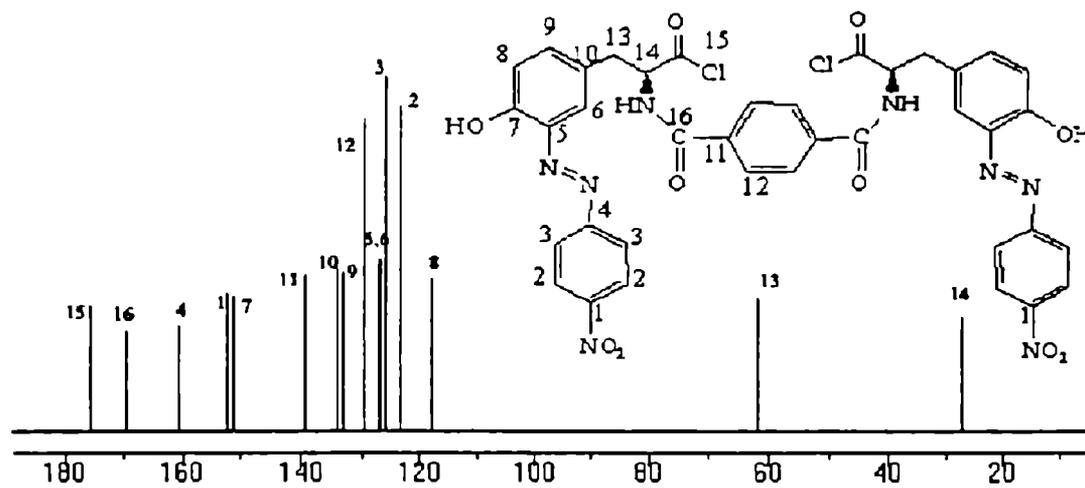
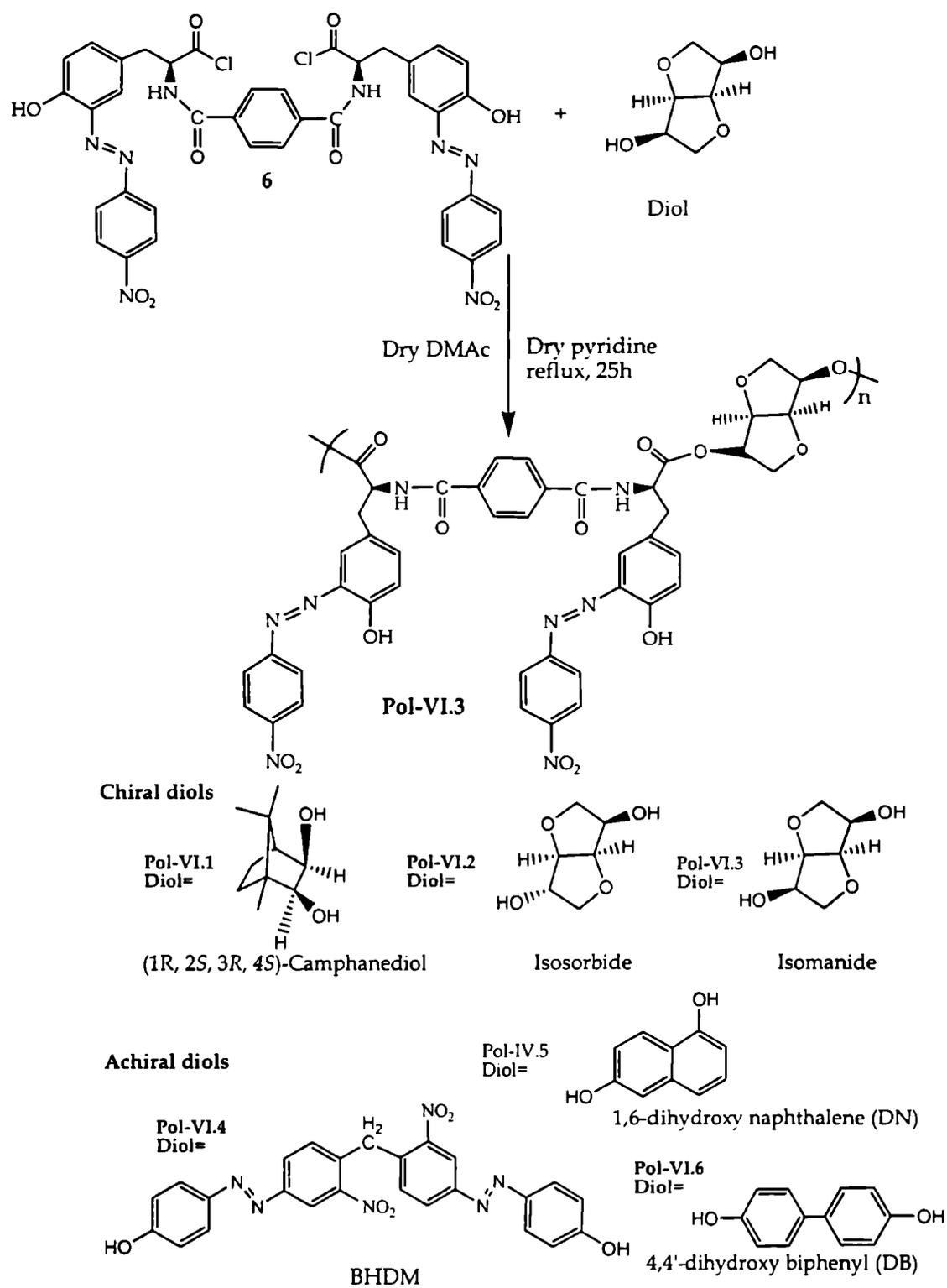


Figure 6.9. ^{13}C NMR spectrum of TYTECl

6.4.2. Synthesis of Poly (ester-amide) s



Scheme 6.2. Synthesis of poly (ester-amide) s

The designed polymer structures were synthesized by the polycondensation of L-tyrosine based chromophore with the diols. All polymer syntheses were done in solution method at high temperatures. Appropriate acid chloride was dissolved in extremely dry dimethyl acetamide (HPLC grade, s. d. fine). To this solution, (S)-2-terephthalamido-3-(3-(4-nitrophenylazo)-4-hydroxyphenyl) propanoic acid chloride (TYTECl, 6) in DMAc was added. Few drops of extremely dry pyridine (99.99% dry pyridine, s.d.fine) were added as acid acceptor. The mixture was refluxed under stirring for 25h. The product was precipitated from cold methanol and washed continuously with hot water, methanol and acetone. After filtration and drying a brown solid was obtained. **Scheme 6.2** gives the synthetic route for polymers.

6.4.2.1. Characterization of polymers

Pol-VI.1

Yield: 70%

Spectral properties

UV λ_{\max} (solid): 362 ($\pi \rightarrow \pi^*$, N=N), 323 ($n \rightarrow \pi^*$, NO₂)

IR(KBr pellet) cm⁻¹ : 3419 (NH st, OH st), 2921 (-CH stretch in camphanediol), 1729 (aromatic ester carbonyl), 1689 (amide I carbonyl stretch), 1532 (NO₂ st as, amide II st sy), 1425 (-N=N- st), 1350 (NO₂ st sy)

¹H NMR (300 MHz DMSO-d₆): δ 9.0 (phenolic -OH), 8.35 (aromatic, near to NO₂), 7.88 (aromatic hydrogen from acid chloride near to -CO), 7.17 (amino acid phenyl ring near to -CH₂), 6.72 (amino acid phenyl ring near to -OH), 4.86 (m, -CH), 4.28, 4.35 (d, -CH₂), 3.13 (m, -CH₂ cyclopentane ring of camphanediol), 2.41 (m, -CH, cyclopentane ring of camphanediol), 2.13 (s, -CH₃ of camphanediol), 1.25 (s, bridged -C(CH₃)₂ of camphanediol).

Pol-VI.2 and Pol-VI.3

Pol-VI.2 (Yield 69%) and **Pol-VI.3** (yield 73%) are different only in the stereochemistry of the chiral building units. So their spectral patterns are similar except in ¹H NMR. But in ¹H NMR the -CH protons which have the different stereochemistry in isosorbide and isomanide appeared as multiplet. So a distinction between them is difficult

Spectral properties

UV λ_{\max} (solid): 362 ($\pi \rightarrow \pi^*$, N=N), 323 ($n \rightarrow \pi^*$, NO₂)

IR (KBr pellet) cm⁻¹ : 3410 (NH st, OH st), 2925 (-CH stretch in isosorbide or isomanide unit), 1731 (aromatic ester carbonyl), 1690 (amide I carbonyl stretch), 1533 (NO₂ st as, amide II st sy), 1424 (-N=N- st), 1345 (NO₂ st sy)

¹H NMR (300 MHz DMSO-d₆): δ 8.9 (phenolic -OH), 8.33 (aromatic, near to NO₂), 8.11(4H aromatic, near to -N=N-), 7.82 (aromatic hydrogen from acid chloride near to -CO), 7.31 (amino acid phenyl ring near to -N=N-), 7.14 (amino acid phenyl ring near to -CH₂) 6.71 (amino acid phenyl ring near to -OH), 4.79(-CH), 4.19, 4.27 (-CH₂), 4.13 (-CH isosorbide or isomanide unit), 3.51 (-CH₂ in isosorbide or isomanide unit), 3.32 (bridge CH in isosorbide or isomanide unit)

Pol-VI-4

Yield: 72%

Spectral properties

UV λ_{\max} (solid): 274 (-Ph-CH₂-Ph-), 362 ($\pi \rightarrow \pi^*$, N=N), 323 ($n \rightarrow \pi^*$, NO₂)

IR (KBr pellet) cm⁻¹ : 3413 (NH st, OH st), 1730 (aromatic ester carbonyl), 1685 (amide I carbonyl stretch), 1530 (NO₂ st as, amide II st sy), 1428 (-N=N- st), 1355 (NO₂ st sy)

¹H NMR (300 MHz DMSO-d₆) δ : 8.88 (phenolic -OH), 8.15 (aromatic, near to NO₂), 7.79 (aromatic hydrogen from acid chloride near to -CO), 7.35 (amino acid phenyl ring near to -N=N-), 7.23 (amino acid benzene ring near to -CH₂) 6.71 (amino acid phenyl ring near to -OH), 5.15 (s, 2H, -CH₂ of BHDM), 4.84(-CH), 4.21, 4.29 (-CH₂)

Pol-VI.5

Yield: 70%

Spectral properties

UV λ_{\max} (solid): 280 (biphenyl), 362 ($\pi \rightarrow \pi^*$, N=N), 323 ($n \rightarrow \pi^*$, NO₂)

IR (KBr pellet) cm⁻¹ : 3390 (NH st, OH st), 1732 (aromatic ester carbonyl), 1687 (amide I carbonyl stretch), 1532 (NO₂ st as, amide II st sy), 1425 (-N=N- st), 1350 (NO₂ st sy)

¹H NMR (300 MHz DMSO-d₆) δ : 8.92 (phenolic -OH), 8.19 (aromatic, near to NO₂), 7.79 (aromatic hydrogen from acid chloride near to -CO), 7.34 (aromatic, biphenyl) 7.29

(amino acid phenyl ring near to -N=N-), 7.19 (amino acid phenyl ring near to -CH₂), 6.59 (amino acid phenyl ring near to -OH), 6.49 (aromatic biphenyl), 4.81(-CH), 4.26, 4.35 (-CH₂).

Pol-VI-6

Yield: 73%

Spectral properties

UVλ_{max} (solid): 362 (π→π*, N=N), 323 (n→π*, NO₂)

IR (KBr pellet) cm⁻¹ : 3393 (NH st, OH st), 1730 (aromatic ester carbonyl), 1685 (amide I carbonyl stretch), 1530 (NO₂ st as, amide II st sy), 1423 (-N=N- st), 1349 (NO₂ st sy), 800-760 (characteristic of naphthalene)

¹H NMR (300 MHz DMSO-d₆) δ: 8.81 (phenolic -OH), 8.22 (aromatic, near to NO₂), 7.73 (aromatic hydrogen from acid chloride near to -CO), 7.21, 7.31 (aromatic, naphthalene), 7.45 (amino acid phenyl ring near to -N=N-), 7.21 (amino acid benzene ring near to -CH₂), 6.80 (aromatic, naphthalene) 6.63 (amino acid phenyl ring near to -OH), 4.76(-CH), 4.19, 4.28 (-CH₂)

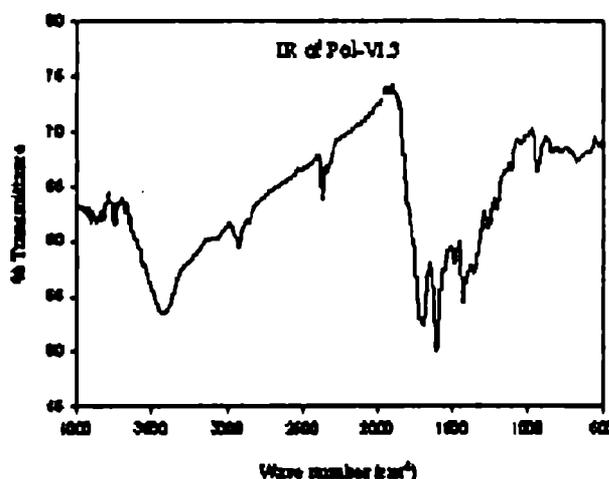


Figure 6.10. IR spectrum of Pol-VI.3

IR spectrum (Figure 6.10) of the polymers have shown two distinct carbonyl peaks at 1730-1715 cm⁻¹ and 1680-1700 cm⁻¹. These peaks can be attributed due to aromatic ester carbonyl and due to amide linkage. In the amide linkage -CO is directly connected to -NH. This decreases the frequency of C=O st. to a lower value than the ester carbonyl. Presence of two distinct

carbonyl peaks confirmed the esterification of TYTCl with different diols. ¹H NMR spectrum is given in Figure 6.11. The poly (ester-amide) s is less soluble in DMSO. So ¹³C NMR spectra could not able to be recorded. Under the percent level of sophistication a

variable solid state ^{13}C NMR spectra of this series of poly (ester-amide) s could not be recorded

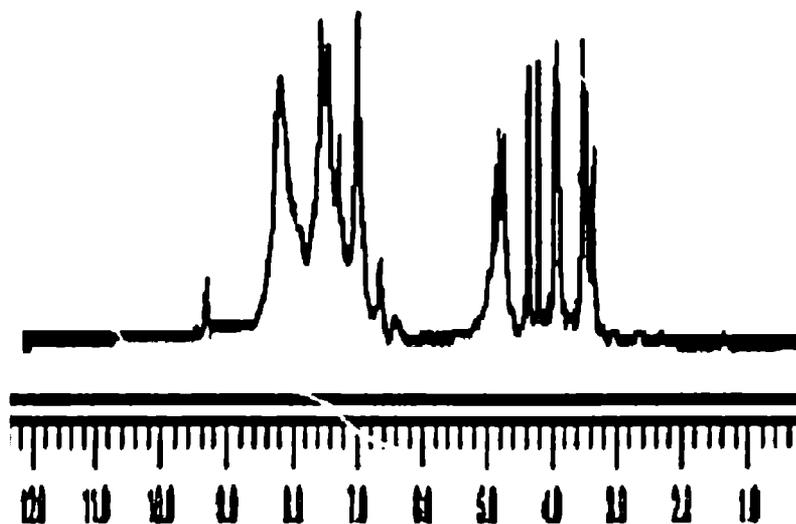


Figure 6.11. ^1H NMR spectrum of Pol-VI.3

Mass spectrum: The mass spectrum (Figure 6.12) of Pol-VI.4 ($m/e = 10016$) gives an idea about the degree of polymerization. It showed that 8 repeating units (one repeating unit = 1252) was involved in the polymerization.

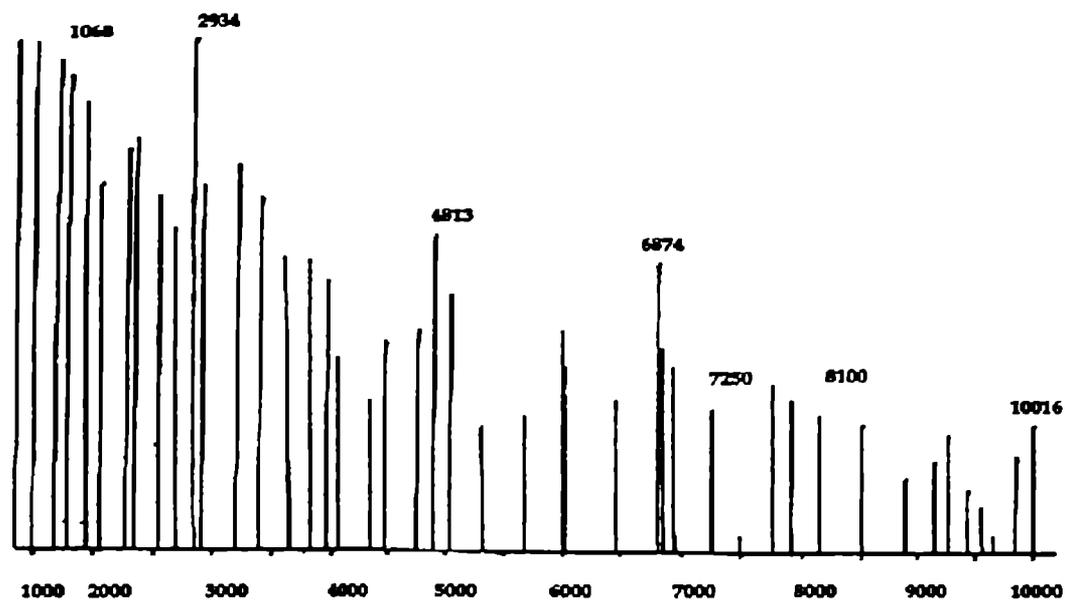


Figure 6.12.. Mass spectrum of Pol-VI.4

6.4.2.2. Thermal properties of the polymers

T_g of side chain azo polymers are low compared to the main chain azo polymers. This may be due to the absence of azo groups in the main chain that decreases the polar order. More over, the efficiency of polymerization of side chain azo compounds is less compared to main chain azo compounds. While the main chain azo polymers contain 15 repeating units in the polymer chain, side chain azo polymers have only 8 repeating units in their chain. Hence main chain azo polymers have shown higher polar order compared to side chain azo polymers. The IDT of side chain azo polymers are slightly higher than that of main chain azo polymers indicating that they are thermally stable. Results are given in Table 6.11

6.5. Evaluation of second harmonic generation efficiency

The NLO efficiencies of poly (ester-amide) s were determined with 2-methyl-4-nitroaniline as the standard using Kurtz and Perry method.¹⁹ Measurements were done by the powder method with a Quanta-Ray Nd-YAG laser from Spectra Physics (1064 nm, 10 ns,365mJ/S) integrated over 20 pulse and an average of 10 pulse. The samples were ground and graded with standard sieves to the phase that match the size (100-150

μm) and loaded on cuvette with 1mm thickness. MNA samples used as standards were also powdered and sieved (100-150 μm) after drying under high vacuum. They were also mounted with the same thickness as the polymer sample. The laser beam was directed unfocused onto the sample kept at a 45° angle to the laser beam which provided the phase that match the situation; the emission was collected from the front face of the sample at 90° angle. The SHG signal at 532 nm was detected by Avantes 2048 spectrometer with CCD camera. The results are shown in Table 6.11.

Table 6.11 gives the properties of the synthesized poly (ester-amide) s containing side chain azo group. The poly (ester-amide) s has SHG efficiency higher than MNA. But compared to main chain azo polymers the efficiency is less. This may be ascribed as due to the low polar order and molecular weight of side chain azo polymers compared to the main chain azo polymers derived from the absence of electron donating azo group in the main chain, which also decreases the donor-acceptor efficiency. Thus, the side chain azo polymers have shown lower value of SHG.

Table 6.11: Yield and Properties of Poly (ester-amide) s

<i>Polymer</i>	<i>Diol molecule</i>	<i>Yield (%)</i>	<i>T_g (°C)</i>	<i>IDT (°C)</i>	<i>[α]_D</i>	<i>*SHG Efficiency</i>
Pol-V.1	Camphanediol	71	293.97	291	-24.3	8.53
Pol-VI.1	Camphanediol	70	220.02	293	-16.3	4.49
Pol-V.2	Isosorbide	78	154.27	297	-23.2	7.73
Pol-VI.2	Isosorbide	69	173.63	326	-12.5	6.33
Pol-V.3	Isomanide	75	299.43	287	-20.4	7.93
Pol-VI.3	Isomanide	73	171.40	325	-12.6	6.38
Pol-V.4	BHDM	74	215.67	275	-16.8	8.02
Pol-VI.4	BHDM	72	176.70	325	-10.1	7.49
Pol-V.5	Dihydroxy biphenyl	72	191.89	236	-18.0	7.60
Pol-VI.5	Dihydroxy biphenyl	70	188.21	328	-13.1	6.53
Pol-V.6	Dihydroxy naphthalene	73	197.51	280	-15.9	7.54
Pol-VI.6	Dihydroxy naphthalene	73	170.21	341	-12.8	6.21

* (MNA Reference, SHG efficiency of MNA was taken as 1)

6.6. Conclusion

From the theoretical and experimental studies of polymers containing azo group in the side chain and in the main chain it was observed that the presence of azo group in the main chain increased the second order NLO efficiency. This can be attributed to the higher polar order for the main chain azo polymer. With an increased donor-acceptor strength (by virtue of having efficient push-pull azo group in the main chain) and higher molecular weight, polar order was found to be higher for the main chain azo polymers, which led to their SHG efficiency

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