

THERMAL STUDIES ON POLYTHIOPHENE CONTAINING MESOGENIC SIDE CHAINS

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Series of thiophenes containing mesogenic side chains at the 3rd position are synthesized. The thermal transitions and thermal stability of the synthesized monomers and polymers are studied. The polarizing microscopic studies of synthesized monomers showed nematic liquid crystalline phase and these mesophases further confirmed by differential scanning calorimetric study. The obtained melting and the isotropic temperatures decrease linearly with the increase of aliphatic chain length. The transition temperatures determined from DSC analysis, overlap well with the temperatures obtained from optical microscopy studies. Thermal stability of the compounds is analysed using thermogravimetric studies. Thermal stability of monomers and polymers has been determined by calculating IPDT values. Structural influence on thermal degradation patterns of monomers and polymers are also discussed.

Keywords: conjugated polymers, liquid crystalline materials, polythiophene, thermal stability, thermogravimetry

Introduction

Conjugated polymers are currently receiving much attention in opto-electronics [1]. Polymeric light emitting devices, polymeric lasers belong to the family of opto-electronic devices, which is expected to replace the conventional inorganic devices, and this technology could lead to a magneto-optical system for writing and erasing data from computer hard drives [2]. Among the polymeric emissive materials, functionalized polythiophenes are proven to be better candidates because of their synthetic versatility and solubility [3]. Introduction of liquid crystalline groups into the side chain of the conjugated polymer is expected to afford a higher electrical conductivity and a notable electrical anisotropy [4]. This is because the polymer main chain can be aligned by the virtue of spontaneous orientation of liquid crystalline side chains and further by macroscopic orientation of liquid crystalline domains by thermal annealing or under external force, such as shear stress and electric or magnetic field.

The selection of emissive materials for LEDs, even though primarily depend on fluorescence and electroluminescence (EL) characters, other properties like thermal stability are also important. This is due to the fact that in LEDs, the EL conversion efficiency is around 5% and the remaining electrical energy may dissipate in the form of heat. This thermal energy instantaneously raises the temperature of the emissive layer. Therefore, for PLED applications, it is mandatory that the polymer should have good thermal stabil-

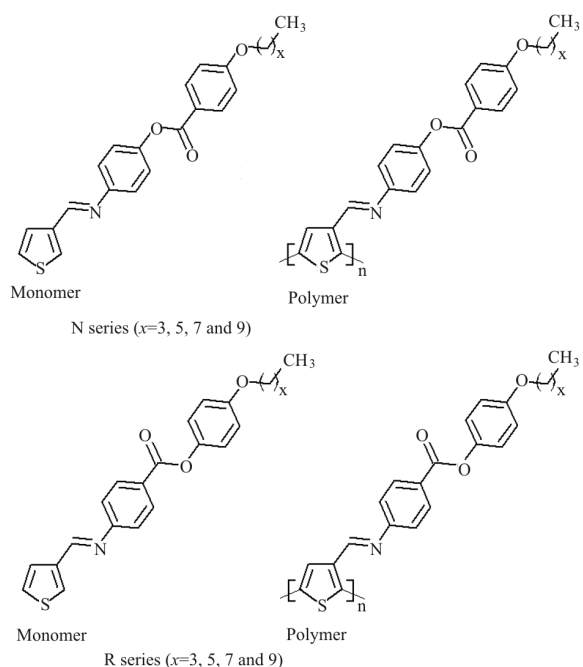
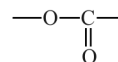


Fig. 1 Chemical structures of N and R series monomers and polymers

ity too [5–9]. In the present study, the thermal behavior of polythiophene model compounds containing phenyl groups linked with azomethine, ester, and alkoxy groups has been studied. The chemical structures of monomers and polymers of varying alkoxy chain length (4, 6, 8 and 10 carbons) are shown in Fig. 1. The N group structures have



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linkages between the phenyl groups, while the R group structures have



linkages. These compounds show polarized electroluminescence in all base color ranges.

Experimental

General method of preparation for thiophenes with side chain bearing mesogens and spacer groups

Preparation of alkoxy benzoyloxy anilines

4-Hydroxy benzoic acid was reacted with alkyl bromide (RBr, $R=4, 6, 8$ and 10) in presence of potassium hydroxide (KOH) in ethanol. The corresponding acid chloride was prepared using SOCl_2 . Then it is coupled with 4-hydroxy nitro benzene. The resulting nitro compound was reduced using tin(II) chloride [10].

Preparation of alkoxy phenoxy amino benzoates

4-Hydroxy phenol was reacted with alkyl bromide (RBr, $R=4, 6, 8$ and 10) in ethanolic KOH and it was coupled with 4-nitro benzoyl chlorides. The resulting compound was reduced using SnCl_2 .

Preparation of Schiff's bases

The amine recovered from above synthesis was dissolved in absolute ethanol and mixed with thiophene-3-carboxaldehyde. The monomer series obtained from the coupling of alkoxy benzoyloxy anilines are called N series and the products obtained from the coupling of alkoxy phenoxy amino benzoates are called R series.

General method of preparation of polymers by electrochemical polymerization

The electrochemical polymerizations of Schiff's bases were carried out in acetonitrile containing tetrabutylammonium hexafluoro-phosphate as the electrolyte. Current density for the polymerization reaction was 2 mA cm^{-2} and the reaction was performed for 3 h. Dedoping of the formed polymers was carried out for about 30 min by reversing the polarity. The time of reaction and dedoping were fixed on the basis of applied current. The above procedure was adopted for synthesizing all polymers. The structure of the all synthesized monomers is confirmed using the NMR and IR spectroscopic techniques.

The different phases obtained for monomers due to thermal transitions were observed using hot stage polarizing microscope. Thermal stability of the compounds was studied using thermogravimetric analysis. All TG experiments were carried out using Netzsch 409C thermogravimetric analyser in nitrogen atmosphere and using a program rate of 10°C . Differential scanning calorimetric studies of monomers and polymers were carried out with the heating rate of $10^\circ\text{C min}^{-1}$ using Perkin Elmer DSC7.

Results and discussion

Molecular structures influence the degree of orientation in soluble poly 3-alkyl thiophenes differing both in side chain length and microstructure [11]. All thiophene monomers synthesized (N and R monomers) are examined using polarizing microscope containing heating/-cooling stage with the heating rate of 10°C . All the monomers showed nematic behavior by exhibiting thread like structures. Table 1 shows the melting and clearing temperatures of these synthesized monomers. In the case of N series monomers, the polarisability, phase stabilization and molecular interactions increase with the increase of alkoxy chain length in aliphatic segment. Overall the melting and the isotropic temperatures decrease linearly with the increase of aliphatic chain length. The molecular packing in solid state depends on the ratio of aliphatic to aromatic segments in the side chain. The melting temperature of R series monomers is high when compared to the corresponding N series monomers. In R series, even though the melting and isotropic temperature decreases, there is no characteristic variation after C_6 in the aliphatic segment and the ΔT decreases with the increase of carbon chain length.

Mesophases can be well characterized by the thermodynamic properties [12]. Hence thermal transitions of all monomers were analysed using differential scanning calorimetry. The transition temperatures obtained from DSC analysis, overlap well with the temperatures obtained from optical microscopy studies. The corresponding transition energies obtained for different transitions are presented in Table 1. The first transition involves higher energy, which is due to the phase transition of crystalline (three dimensional) to nematic phase (uni-dimensional). The second transition-nematic to isotropic transition involves very low energy compared to that of first transition. In R series, the energy does not change up to R8 monomer and then the value decrease with the increase of aliphatic chain length. In R series monomers, energy for the 2nd transition increases with increase of carbon chain length. The DSC analysis was undertaken for N and R series polymers (PN and PR series) and the obtained transi-

Table 1 Melting and clearing temperatures of thiophene based liquid crystalline monomers and polymers

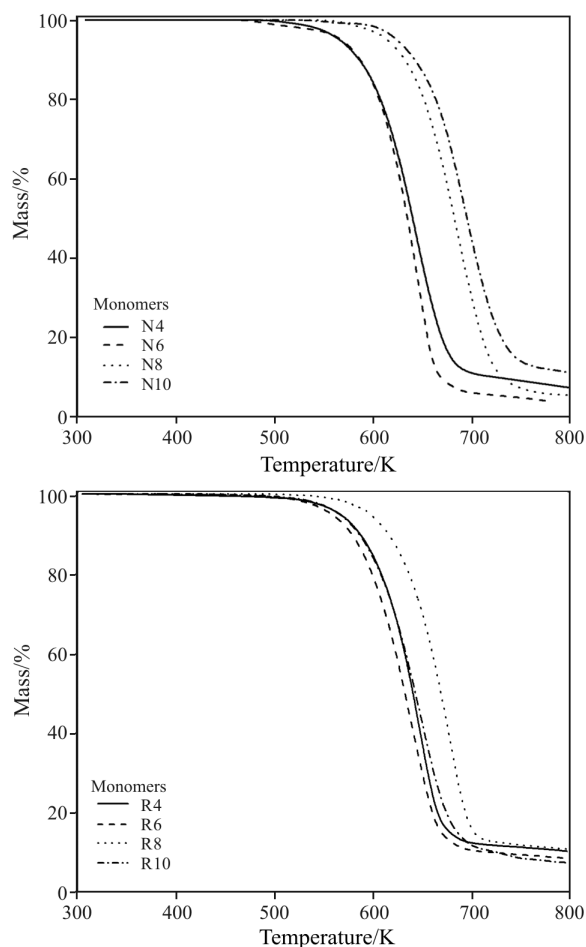
Compound	Melting temperature		Clearing temperature		ΔT ($T_m - T_c$)/°C	
	T_m /°C	$E/J\text{ g}^{-1}$	T_c /°C	$E/J\text{ g}^{-1}$		
Monomer	N4	124	58	152	28	
	N6	113	72	148	35	
	N8	99	56	140	41	
	N10	91	63	138	47	
	R4	133	83	146	13	
	R6	111	82	123	12	
	R8	117	84	135	8	
	R10	111	53	128	17	
Polymer	N4	102	1.4	139	0.04	37
	N6	102	1.5	138	0.07	36
	N8	102	1.4	139	0.02	37
	N10	102	3.2	140	—	38
	R4	102	1.6	139	0.03	37
	R6	102	3.0	129	0.05	27
	R8	102	3.4	134	—	32
	R10	102	2.6	139	0.03	37

tion temperatures, and the energies involved in these transitions are presented in Table 1. The results show that in polymers, irrespective of the linkage, the 1st transition temperature is same. But the energy involved with this transition varies with carbon chain length. Like R10 monomer, R10 polymer also shows less energy for 1st transition compared to R8.

Thermogravimetry is a powerful tool in assessing thermal stability of polymers [13–15]. Thermal stability of the compounds is monitored using thermogravimetry and the results are used to compare the thermal stability of different structures of thiophene monomers and polymers. The obtained curves for monomers of N and R series are presented in Fig. 2. The monomers of N series are stable up to 500 K. Major loss starts around 550 K for N4 and N6 and both the compounds are stable up to 610 K. In the case of monomers of R series, it is observed that all the monomers are stable up to 500 K and the major mass loss starts at 550°C. R8 shows slightly better stability than R10.

The observed initial decomposition temperature (IDT) is presented in Table 2. The monomers of N8 and R8 show high value of initial decomposition temperature. In comparison to R series, N series monomers start decomposing at higher temperatures. The maximum decomposition temperature found to be high in the case of N8 and N10. In the R series, R8 is showing high value of D_{\max} . The results on IDT and D_{\max} suggest that N8 and N10 monomers are thermally stable than other monomers and in the case of R series R8 showing higher stability than others.

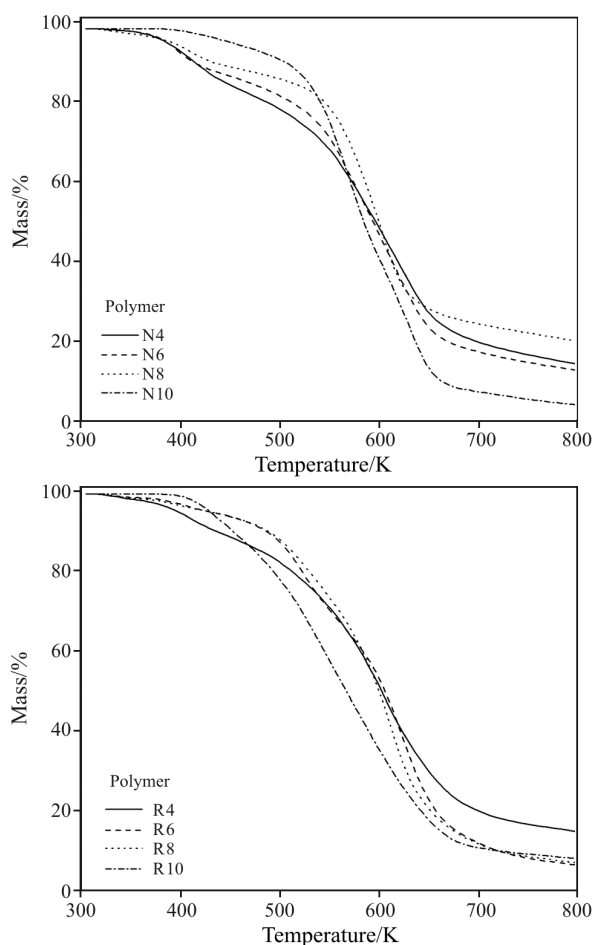
Thermal stability of R and N series polymers (PN and PR series) is studied using thermogravimetric analysis and the curves are presented in Fig. 3. The observed initial decomposition temperature (IDT) is presented in Table 3. IDT increases with the

**Fig. 2** TG curves of N and R monomers

increase of alkoxy chain length in both N and R series. PN10 shows highest stability based on IDT. On comparing IDT of polymers of N and R series, PN4 and PN6 show more thermal stability than PR4

Table 2 Thermal behaviors of N and R series monomers

Monomer	IDT/K	D_{\max} /K	IPDT/K	Temperature at mass loss%/K				
				20%	40%	60%	80%	90%
N4	511	651	616	610	634	647	668	720
N6	486	643	605	607	631	640	654	669
N8	569	695	657	654	676	689	709	730
N10	557	695	675	665	685	706	730	848
R4	463	649	617	610	633	649	664	697
R6	490	638	613	600	624	642	659	681
R8	544	681	647	638	661	678	693	725
R10	501	655	612	609	634	653	673	697

**Fig. 3** TG curves of R and N polymers

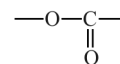
and PR6. In the case of calculated maximum decomposition temperature (D_{\max}), the value decrease with the increase of alkoxy chain length.

Integral procedural decomposition temperature (IPDT) as proposed by Doyle provides a semi-quantitative means for comparison of relative thermal stabilities [16, 17]. The integral procedural decomposition temperature is derived as a means of summing up the whole shape of the normalized data curve. IPDT ac-

counts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve. Thus thermal stability of these monomers and polymers has also been determined by calculating IPDT values. To place all materials on an equal procedural footing, the curve is integrated on the basis of the total experimentally accessible temperature ranges. The area under the curve divided by the total area is the total curve area, A^* , is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, T_{A^*} , by

$$T_{A^*} = (T_{\text{end}} - T_{\text{ini}})A^* + T_{\text{ini}} \quad (1)$$

T_{A^*} represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing X -axis upto T_{A^*} and the Y -axis mass fraction remaining at T_{end} . K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in Eq. (1). This index, the integral procedural decomposition temperature is a reproducible datum having practical significance as an integrated half-volatilization temperature. The calculated IPDT value for the monomers and polymers are respectively presented in Tables 2 and 3. In general, in N series monomers, as the chain length increases the IPDT also increases and hence the thermal stability also increases. Overall the IPDT of N10 and R8 are higher than all others of its respective homologs. The presence of



link (present in N-series) stabilizes the molecule than



link present in R series.

In the case of polymers of N series, PN10 shows high value of IPDT and the value increases from PN4

Table 3 Thermal behavior of N and R series polymers

Polymer	IDT/K	D_{\max} /K	IPDT/K	Temperature at mass loss%/K				
				10%	20%	30%	40%	50%
N4	383	688	615	490	600	648	689	746
N6	385	679	619	524	609	646	681	724
N8	344	667	625	573	628	655	680	820
N10	430	622	638	583	613	637	667	698
R4	346	667	624	526	608	654	692	750
R6	368	686	639	554	606	656	689	718
R8	356	673	637	559	616	654	678	709
R10	438	590	607	514	570	611	651	697

Table 4 Effect of structure on the level of degradation at different temperatures

Monomer	Temperature/K	Mass loss/%
N4	616–687	61.8
	687–834	6.8
	834–949	5.8
N6	623–676	56.3
	676–778	4.6
N8	667–735	59.1
	735–930	6.5
	930–980	1.7
N10	667–747	64.9
	747–900	6.3
	900–980	5.4
R4	630–677	51
	677–912	10.1
	912–982	3.3
R6	610–694	66
	694–883	4.7
	883–982	3.8
R8	651–708	60.3
	708–912	6.3
	912–982	3.3
R10	624–698	60.8
	698–877	7.9
	877–984	2.2

to PN8 with the increase of alkoxy chain length. In R series, PR6 showing high value and the addition of alkyl chain length decrease the stability. Comparison of the values obtained for N and R series polymers reveal that R series is showing better stability in terms of IPDT except in PR10 and PN10 is stable than PR10.

The extracted degradation data of monomers and polymers obtained from curves are presented in Tables 2 and 3, respectively. In monomers of N series, the temperature at which 20, 40, 60, 80 and 90% mass loss occurs increase, with the increase of alkoxy chain length. For N4 monomer, 20% of mass loss is observed at 610 K while it occurs at 665 K in N10 monomer.

Table 5 Effect of structure on the level of degradation at different temperatures

Polymer	Temperature/K	Mass loss/%
N4	400–462	6.0
	462–596	11.4
	596–673	16.7
	673–736	13.0
	736–917	7.1
N6	394–435	3.9
	435–585	10.0
	585–658	17.7
	658–730	17.7
	730–918	6.3
N8	406–450	2.9
	450–597	7.4
	597–654	17.2
	654–698	14.9
	698–917	7.8
N10	431–585	10.4
	585–680	32.6
	680–735	14.8
	735–917	4.3
	402–535	8.8
R4	535–629	13.0
	629–763	27.5
	763–917	5.1
	406–532	5.8
	532–660	23.4
R6	660–730	22.2
	730–812	6.7
	812–917	2.4
	394–539	6.1
	539–641	18.9
R8	641–711	24.2
	711–787	7.8
	787–918	3.2
	437–549	14.5
	549–629	18.7
R10	629–749	22.8
	749–918	3.4

The results show that in general, the temperature at which the 10% mass was lost increase with the increase of chain length of N and R polymers. The tem-

perature at which 20, 30 and 40% mass loss was obtained also increases as the chain length increases from N4 to N8. Unlike monomer series, N10 polymer shows degradation at lower temp itself. In the case of R series polymers, no characteristic relation could be understood between the alkoxy chain length and degradation. Similar to that of PN10, PR10 polymer also shows poor thermal stability on the basis of mass loss.

Effect of structure on the level of degradation at different temperatures is given in the Tables 4 and 5 for the monomers and polymers, respectively. All monomers undergo 3-stage degradation except N6 monomer where only two-stage degradation is observed. The polymer PN10 and PR10 undergoes four-stage degradation while other polymers of R and N series undergo 5-stage degradation.

Overall, the obtained results from thermal studies suggest that in monomers, the melting and the isotropic temperatures decrease linearly with the increase of aliphatic segment and the characteristic texture of all monomers are same viz, nematic phase. In polymers, irrespective of the linkage, the 1st transition temperature is same. The thermal stability of N10 and R8 monomers are found is high on the basis of IDT and IPDT. In the case of polymers, the overall thermal stability of the PN10 is high since it exhibits high value of initial decomposition temperature as well as integral procedural decomposition temperature.

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