Poly(dibromophenylene oxide)s Through Atom Transfer Radical Rearrangement Polymerization of Various Transition Metal Complexes

Pinar Camurlu[a]; Duygu Kisakürek[b]

[a] Department of Chemistry, Akdeniz University, Antalya, Turkey [b] Department of Chemistry, Middle East Technical University, Ankara, Turkey

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PINAR CAMURLU[1] and DUYGU KISAKÜREK[2*]

[1] *Akdeniz University, Department of Chemistry, 07058, Antalya, Turkey*
[2] *Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey*

In this study, the synthesis of poly(dibromophenylene oxide)s were achieved via atom transfer radical rearrangement polymerization through decomposition of Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Cu(II)-Cu(TBP)$_2$(NMIZ)$_2$, Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Co(II)-Co(TBP)$_2$(NMIZ)$_2$, Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Ni(II)-Ni(TBP)$_2$(NMIZ)$_2$ complexes. Polymerizations were carried out under two different conditions to investigate the effect of time and temperature on percent conversions, intrinsic viscosities. Characterizations of the polymers were performed by FTIR, DSC,^{1}H-NMR, ^{13}C-NMR, SEM and viscometric measurements. The poly(dibromophenylene oxides)s, synthesized by the transition metal complexes, having nonchelating ligand N-methyl imidazole, displayed selectivity in the favor of 1-2 and 1-4 additions, taking place at equal rates irrespective of the type of the metal used. Among the synthesized polymers, the highest percent conversion and intrinsic viscosity was achieved by the decomposition of Cu(TBP)$_2$(NMIZ)$_2$ complex, whereas, Ni(TBP)$_2$(NMIZ)$_2$ yielded the lowest. Investigation of the complexes via mass spectroscopy and the thermal behavior of the by-products enlightened the underlying reasons of the variations at percent conversion and intrinsic viscosity values of the resultant polymeric products.

Keywords: Poly(dibromophenylene oxide), transition metal complexes, atom transfer radical rearrangement polymerization, solid state polymerization

1 Introduction

Poly(dihalophenylene oxide)s has been synthesized in various forms since 1916 because of their mechanical, chemical and thermal properties. The original synthesis was achieved by Hunter and his colleagues through the ethyl iodide–induced decomposition of anhydrous silver 2,4,6 trihalophenoxide (1). In 1962 Blanchard et al. (2) showed the possibility to polymerize 4-halo-2,6-dimethylphenols into high molecular weight poly(2,6-dimethylphenylene ether)s by the action of cupric ions, providing pyridine is also present. It was observed that this reaction requires a stoichiometric amount of cupric ions and proceeds through the pyridine complexes of cupric phenolates. For this reason, preparation and characterization of bis(phenolato)bispyridine copper(II) complexes, as well as their decomposition yielding poly(dihalophenylene oxide), was also performed. Later Harrod et al. (3–7) and

Kısakürek et al. (4, 6, 8–12) revealed much progress in understanding the mechanism of the reaction.

The proposed mechanism in 1973 (3) involved the following several key steps where a fast induced decomposition of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) via a radical to give Cu(I) complex and radical substituted 2,4,6-trichlorocyclohexadienone occurs. Secondly, 2,4,6-trichlorocyclohexadienone slowly dissociate in to initiator and a 2,4,6-trichlorophenoxy radical forms, which could be the reason for chain branching. Thirdly, abstraction of a chlorine atom from 2,4,6-trichlorocyclohexadienone occurs where Cu(I) gives Cu(II) and a substituted phenoxy radical. This mechanism was modified (4) in 1981 as a result of ^{13}C-NMR studies. The final proposal provided by Kısakürek et al. (11, 12) involves a similar mechanism which concludes the reaction to be atom transfer radical rearrangement polymerization.

Up to date polymerization of halogenated phenols has been studied with transition and inner transition metal complexes with various amine ligands through various decomposition techniques which are electroinitiation in solution (13), thermal decomposition in solid state (14) and in solution (15). Although there have been several attempts

*Address correspondence to: Duygu Kısakürek, Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey. E-mail: duygu@metu.edu.tr

to synthesize poly(chlorophenylene oxide)s utilizing several different amine ligands, success was achieved only via solid state decomposition of Cu(DCP)$_2$(NMIZ)$_2$ (16). Thus, authors considered the use of N-methylimidazole ligand as a powerful approach to archive better percent conversions.

As a part of a broader study, the effect of NMIZ and type of the transition metal on structure, molecular weight, percent conversion and Tg's of the poly(dibromophenylene oxide)s synthesized through Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Cu(II) (Cu(TBP)$_2$(NMIZ)$_2$), Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Co(II) (Co(TBP)$_2$(NMIZ)$_2$) and Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Ni(II) (Ni(TBP)$_2$(NMIZ)$_2$) complexes were investigated.

2 Experimental

2.1 Materials

Analytical grade 2,4,6-tribromophenol (Aldrich Chemical Co. Ltd.) was used without further purification. The reagent grade N-Methyl imidazole (Merck) was used as ligand in the preparation of the complexes. Commercially available reagent grade copper sulphate pentahydrate; (CuSO$_4$.5H$_2$O), cobalt sulphate heptahydrate; (CoSO$_4$.7H$_2$O), nickel sulphate hexahydrate; (NiSO$_4$.6H$_2$O) (Merck) were used for the preparation of complexes. Synthesis and characterization of the complexes is provided in the literature (17, 18).

2.2 Instrumentation

Viscosity of the polymers was measured in toluene at 30°C by using Schott Gerate AVS 400 model automatic viscometer equipped with Schott Gerate CT 1150 model thermostat. Thermal behavior of the complexes and glass transition temperatures of the polymers were obtained by a Dupont thermal analyst 2000 DSC 910S model differential scanning calorimeter with 10°C/min for a 7 mg sample. Treatment of the polymer and complex samples were performed under nitrogen and air atmosphere, respectively. Infrared spectra of the complexes and the polymers were recorded on a Mattson 1000 model FTIR spectrometer by dispersing the sample in KBr pellets.^{1}H and ^{13}C-NMR spectra of samples were recorded by using a BRUCKER Instruments, Avance Series (DPX 400), 400 MHz High Performance Digital FT-NMR Spectrometer. Deuterated chloroform was used as the solvent and TMS as an internal reference. Complexes were subjected to Mass Spectroscopy (MS) (LC/MC Platform II Micromass UK (Electron Impact) mass spectrometer) to characterize the weight loss during solid state polymerization of the complexes.

2.3 Polymer Synthesis

During the synthesis of polymers, about 4 g of the complex was placed into a glass sample holder (3.5 cm in height and 3 cm in diameter) and decomposed under predetermined temperature and time conditions. The decomposed product was allowed to cool to room temperature in a desiccator and then weighed to determine the weight loss during the thermal decomposition. The decomposed complex was dissolved in toluene and after removing the undissolved by-product, (NMIZ)$_2$MBr$_2$, poured into a large amount of ethyl alcohol containing a few drops of concentrated HCI. Then, the precipitated polymer was filtered, washed with ethyl alcohol, and dried till a constant weight under vacuum.

Synthesis of the polymers through the thermal polymerization of the complexes results in a weight loss of the initial complex due to the formation of gaseous products. Hence, complexes were subjected to mass spectroscopy to investigate the origin of the gaseous products where such results could be useful in understanding the relation between the weight loss and % conversion. According to the mass spectroscopy study, (Table 1) the gaseous products originated from the loss of a mainly halogenated phenol and to some extent, from the neutral amine ligand (19).

Solid state thermal polymerization of Cu(TBP)$_2$(NMIZ)$_2$, Co(TBP)$_2$(NMIZ)$_2$ and Ni(TBP)$_2$(NMIZ)$_2$ complexes were performed under two different conditions. In the first condition, time kept constant at 3 h and temperature varied between 100°C to 250°C. Under the second condition, the temperature was kept constant at maximum conversion temperature and the time varied from 3 to 48 h. The calculated yields for the polymerizations were based on the initial weight of the complexes; since the ligand and metal do not incorporate into the polymer, the results may appear to be low in value. For all syntheses, the percent conversion and the weight loss were calculated as follows;

$$\% \, \text{Conversion} = \frac{\text{Weight of the polymeric product}}{\text{Initial weight of the complex}} \times 100$$

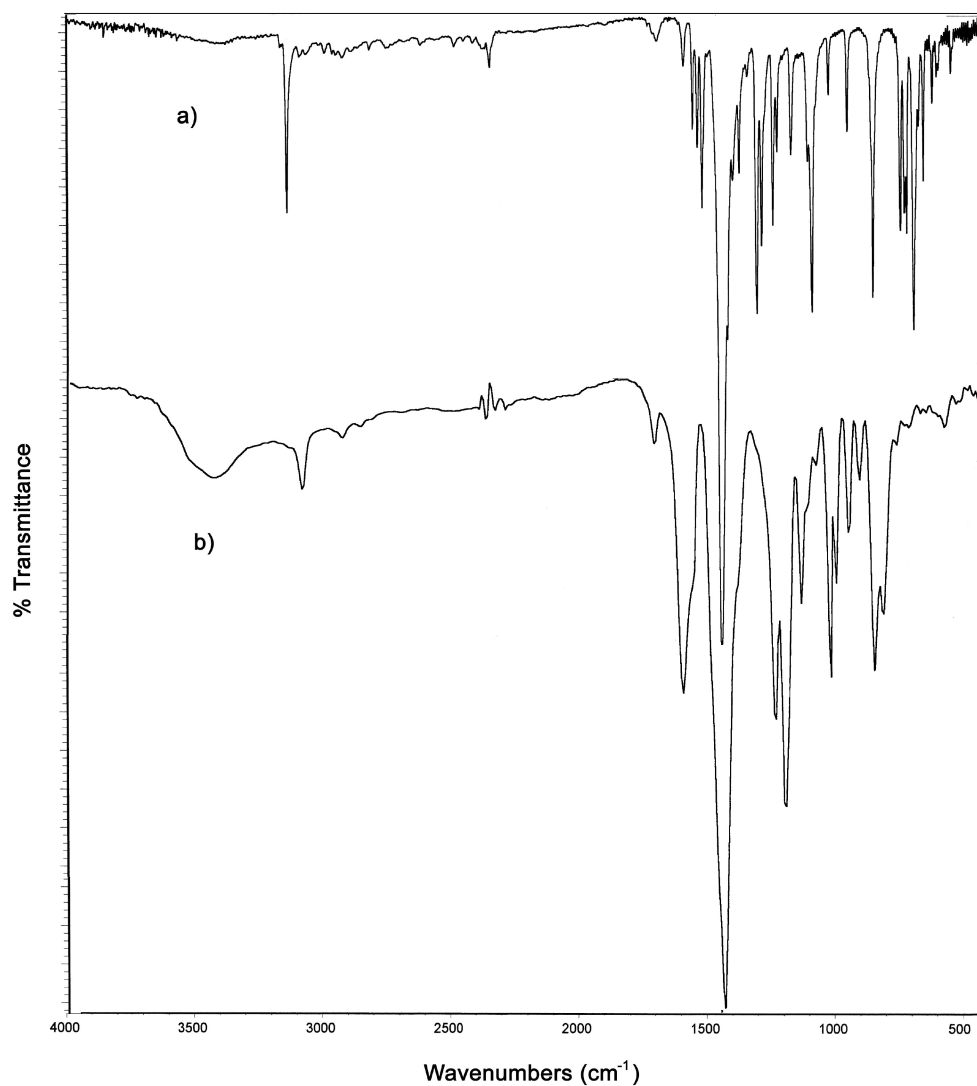Weight loss = Initial wt of complex − wt of the products after decomposition

$$\% \, \text{Weight loss} = \frac{\text{Weight loss}}{\text{Initial weight of the complex}} \times 100$$

3 Results and Discussion

The polymer formation was followed by the FTIR through the appearance of the new peaks around 950–1030 cm^{-1} due to formation of the etheric bond during the polymerization (Figure 1(a,b)). The polymers were characterized by the C=C stretching at 1380, 1440, 1560 and 1610 cm^{-1}; C-O-C stretching at 950, 1006 and 1033 cm^{-1}; C-O stretching at 1030–1245 cm^{-1}; out-of-plane C-H bending at 820 and

**Table 1.** MS data for Ni(TBP)$_2$(NMIZ)$_2$ and Cu(TBP)$_2$(NMIZ)$_2$ (The acceptable error limit in data evaluation is $\pm$ 2 units).

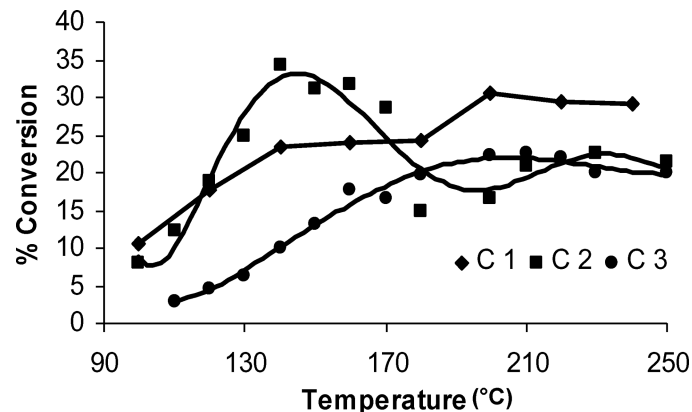| *Ni(TBP)$_2$(NMIZ)$_2$*			*Cu(TBP)$_2$(NMIZ)$_2$*		
Relative intensity %	*M/Z*	*Possible origin of the peak*	*Relative intensity %*	*M/Z*	*Possible origin of the peak*
100	90	TBP	100	91	TBP
23.37	81	NMIZ	22.4	81	NMIZ
18.49	327	TBP	16.5	327	TBP
12.62	141	TBP	10.8	41	NMIZ
11.83	41	NMIZ	10.7	42	NMIZ
10.80	42	NMIZ	8.1	249	TBP
10.50	40	NMIZ	3.6	220	TBP
2.51	249	TBP	5.5	116	TBP
2.30	220	TBP	13.9	141	TBP

Fig. 1. FTIR Spectrum of the a) Cu(TBP)$_2$(NMIZ)$_2$ complex and, b) polymer obtained through thermal decomposition.
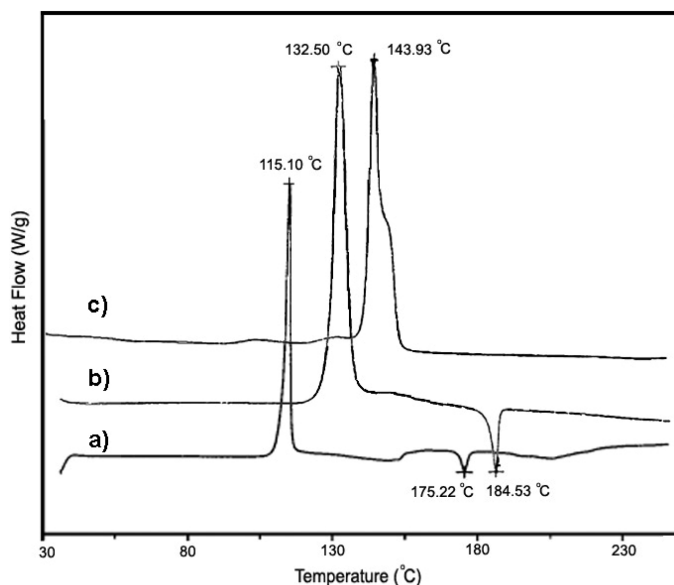
Fig. 2. DSC Thermograms of a) Cu(TBP)$_2$(NMIz)$_2$-(C1), b) Co(TBP)$_2$(NMIz)$_2$-(C2), c) Ni(TBP)$_2$(NMIz)$_2$-(C3) by heating rate of 10°C/min.
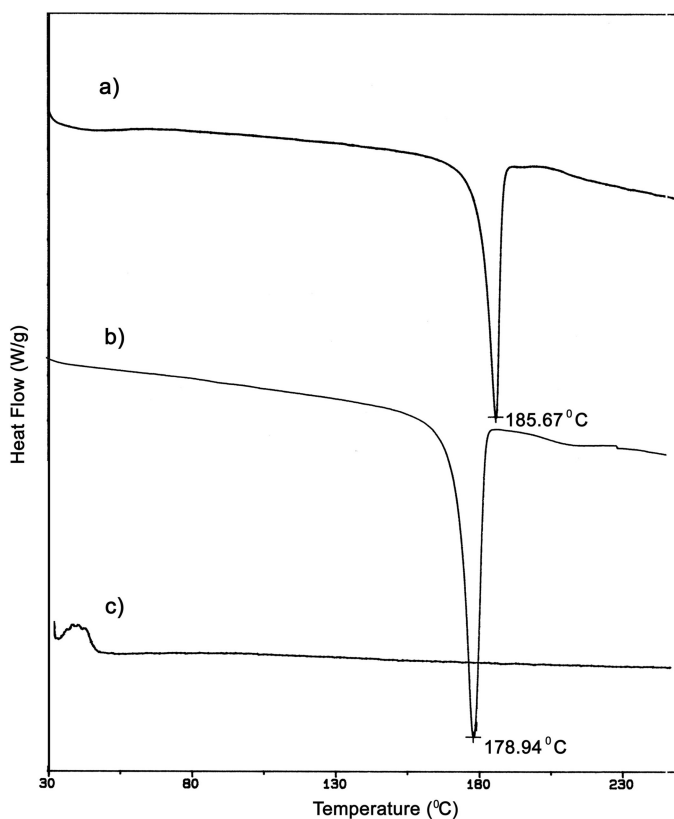
Fig. 3. DCS thermograms of the by-product produced from the decomposition of a) Co(TBP)$_2$(NMIZ)$_2$, b) Cu(TBP)$_2$(NMIZ)$_2$ and, c) Ni(TBP)$_2$(NMIZ)$_2$ complexes.

Fig. 4. % Conversion vs. temperature graph of Cu(TBP)$_2$(NMIZ)$_2$-(C1), Co(TBP)$_2$(NMIZ)$_2$-(C2) and Ni(TBP)$_2$(NMIZ)$_2$-(C3) complex at constant decomposition time (3 h).

850 cm^{-1} and C-H stretching of benzene ring at 3079 cm^{-1}. The peak around 3500 cm^{-1} signified the phenolic end group of the polymer.

Thermal behaviors of the complexes were investigated by DSC measurements under atmospheric conditions for all complexes in order to achieve the normal polymerization conditions. A sharp exothermic peak at 116.88°C and two endothermic peaks at 171.95°C and 205.83°C were observed in DSC thermograms of Cu(TBP)$_2$(NMIZ)$_2$ (Figure 2(a)). Co(TBP)$_2$(NMIZ)$_2$ complexes (Figure 2(b)) showed a sharp exothermic peak at 132.5°C and an endothermic peak at 184.53°C, whereas Ni(TBP)$_2$(NMIZ)$_2$ (Figure 2(c)) showed a single sharp exothermic peak at 143.93°C. The exothermic peaks are attributed to the new bond formation during polymerization. This vision was previously supported by DSC-IR study (16) which showed the polymer formation at the peak temperature and the increase in the % conversions during polymerization beyond the exothermic peak temperatures. In order to investigate the origin
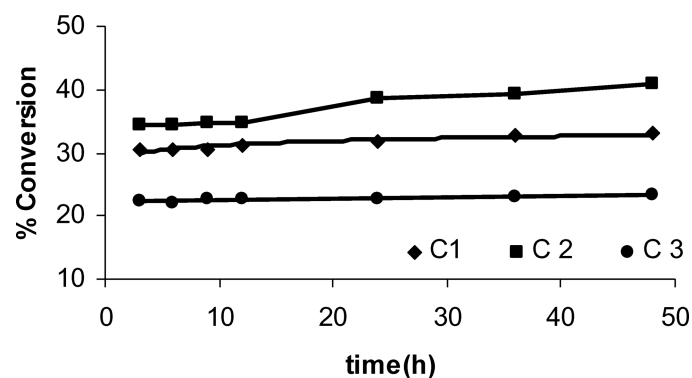
Fig. 5. % Conversion vs time graph of Cu(TBP)$_2$(NMIZ)$_2$-(C1), Co(TBP)$_2$(NMIZ)$_2$-(C2) and Ni(TBP)$_2$(NMIZ)$_2$-(C3) complex at constant temperature (200°C, 140°C and 210°C, respectively).
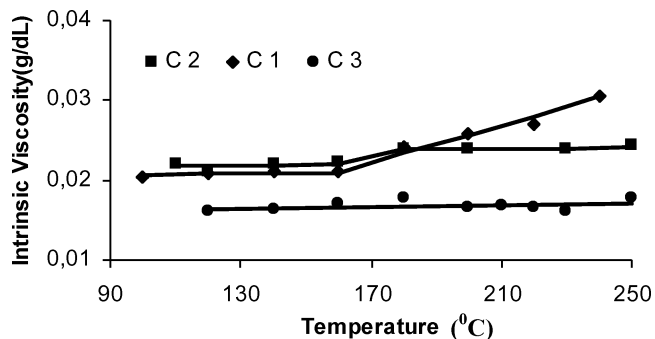
Fig. 6. $[\eta]$ vs. Temperature graph of polymer obtained from Cu(TBP)$_2$(NMIZ)$_2$-(C1),Co(TBP)$_2$(NMIZ)$_2$-(C2) and Ni(TBP)$_2$(NMIZ)$_2$ -(C3) complex at constant decomposition time (3 h).
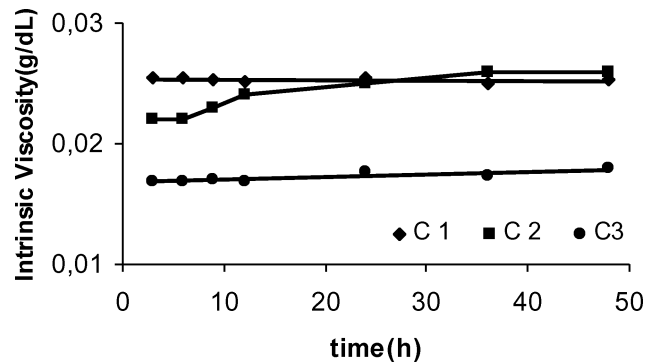
Fig. 7. $[\eta]$ vs. time graph of polymer obtained from Cu(TBP)$_2$(NMIZ)$_2$-(C1), Co(TBP)$_2$(NMIZ)$_2$-(C2) and Ni(TBP)$_2$(NMIZ)$_2$-(C3) complex at a constant temperature (200°C, 140°C and 210°C, respectively).

of the endothermic peaks, authors investigated the thermal behavior of the by-products formed during the polymerization (Figure 3). The by-products achieved due to polymerization of Cu(TBP)$_2$(NMIZ)$_2$ and Co(TBP)$_2$(NMIZ)$_2$ complexes revealed endotherms that were close to the values reflected in thermograms of the original complexes (Figure 2). Hence, those endotherms were attributed to the phase transformation (melting) of the by-products.
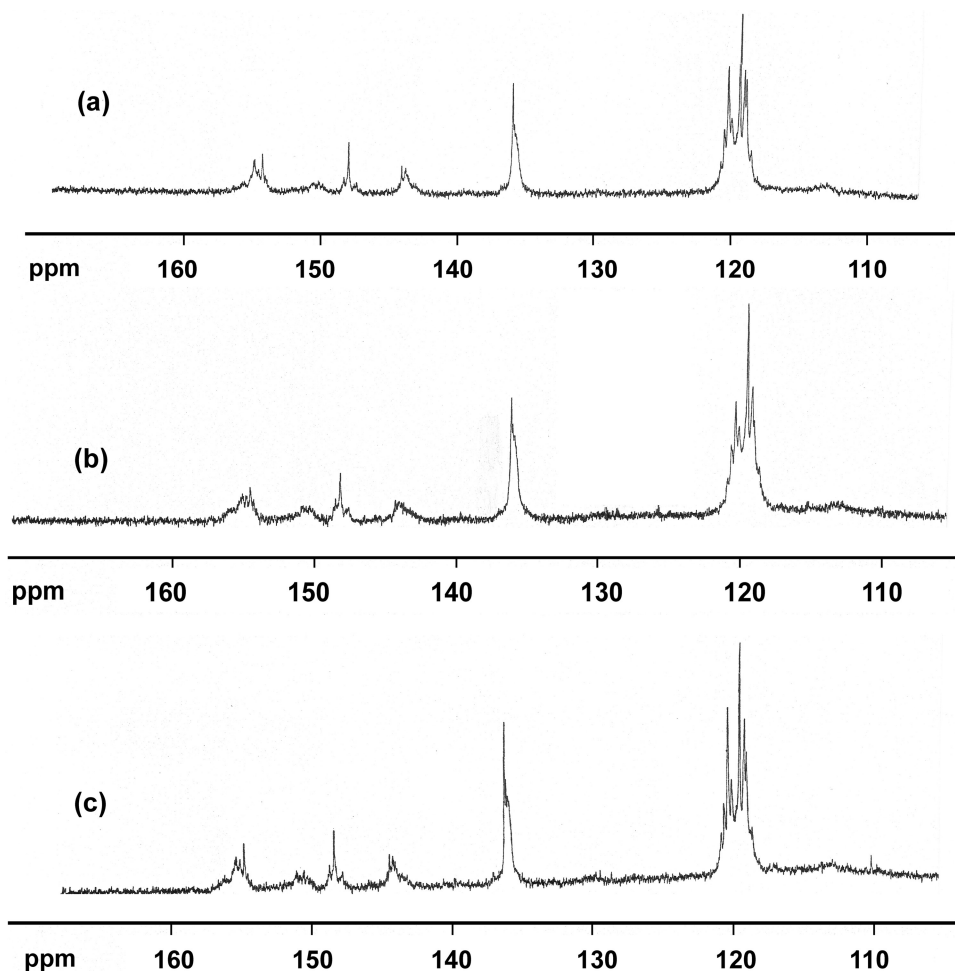
Fig. 8. ^{13}C-NMR Spectrum of the polymer obtained from the decomposition of a) Cu(TBP)$_2$(NMIZ)$_2$, b) Co(TBP)$_2$(NMIZ)$_2$, and, c) Ni(TBP)$_2$(NMIZ)$_2$.

During the synthesis of the polymer through $Cu(TBP)_2$ $(NMIZ)_2$ by atom transfer radical rearrangement polymerization, as the temperature increased, percent conversion increased and reached a maximum value of 30.6% at 200°C, followed by a slight decrease (Figure 4). The high temperature behaviour could be related to the increase in the weight losses. MS study revealed the original source of the weight loss as the loss of halogenated phenol during thermal decomposition which could be considered as the underlying reason of the decline in the % yield during polymerizations at high temperatures. When the temperature was kept constant at a maximum conversion temperature of 200°C, and the time varied from 3 to 48 h, both percent conversion and weight loss increased slightly (Figure 5).

The maximum conversion value of 34.4 % was achieved at 140°C in the case of the $Co(TBP)_2(NMIZ)_2$ complex.

As the temperature increased, percent conversion increased up to 140°C, and then decreased to 21.3% till to the melting point (184.53°C, corresponding to the melting of the by-products, confirmed by DSC). An increase in temperature beyond the maximum percent conversion temperature (140°C) decreased the percent conversion in $Co(TBP)_2(NMIZ)_2$, which could be attributed to the hindrance of the diffusion of the monomers due to both the formation of a large amount of by-product, $(NMIZ)_2MBr_2$ and the increase in percent weight loss. Beyond the melting point of the by-product, percent conversion gradually increased. This inspection could be related to the ease of diffusion in the molten state. At 140°C, different decomposition times between 3 and 48 h were performed where longer than 12 h decomposition time resulted in an increase in percent conversion (Figure 5).
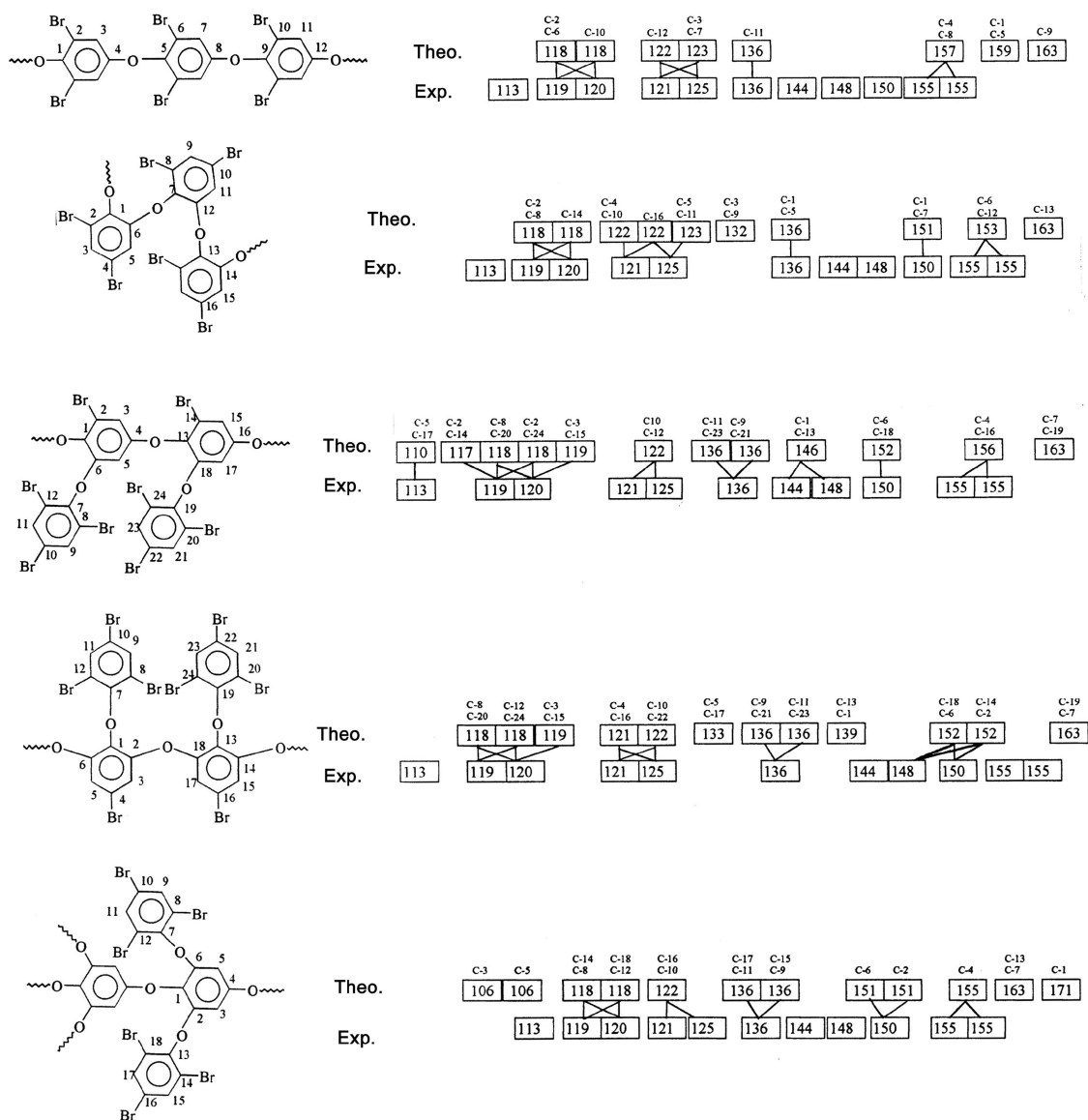

Fig. 9. ^{13}C-NMR shift data of the polymer obtained from $Cu(TBP)_2(NMIZ)_2$ complex.

In the case of Ni(TBP)$_2$(NMIZ)$_2$, there was a sharp increase in percent conversion up to 210°C followed by a slight decrease to 19.9% while approaching 250°C. This observation could again be related to the weight losses, which mainly originated from halogenated phenol itself. The maximum conversion value of 22.4% was achieved at 210°C (Figure 4). Percent weight loss increased gradually as the polymerization temperature approached to 250°C. At 210°C, an increase in decomposition time had no effect on percent conversion of Ni(TBP)$_2$(NMIZ)$_2$ (Figure 5).

Generally, all the synthesized polymers revealed low intrinsic viscosity, indicating the high degree of branching of the polymer. This fact was also supported by the ^{1}H-NMR and ^{13}C-NMR studies. The polymers synthesized through the decomposition of Cu(TBP)$_2$(NMIZ)$_2$ had the highest value, whereas Ni(TBP)$_2$(NMIZ)$_2$ had the lowest value of intrinsic viscosity (Figure 6). This observation could be related to the thermal stability of complex (confirmed by DSC), which might lead to lower intrinsic viscosity. The increase in the intrinsic viscosities of the polymers

synthesized by the decomposition of Cu(TBP)$_2$(NMIZ)$_2$ and Co(TBP)$_2$(NMIZ)$_2$ above the melting point of their by-products, could be due to the ease of diffusion of the complex in a molten state. As confirmed by DSC, this effect did not appear in the Ni(TBP)$_2$(NMIZ)$_2$ complex. Hence, lower % conversion and lower molecular weight of the polymer synthesized through a nickel complex relative to copper complex might be related with the difference in their structure and the oxidizing powers of these two metals. Cu(TBP)$_2$(NMIZ)$_2$ and Ni(TBP)$_2$(NMIZ)$_2$ seem to be less affected than Co(TBP)$_2$(NMIZ)$_2$, with the variation of decomposition time (Figure 7). Bis(2,4,6-tribromophenolato)di(pyridine)Co(II) and Bis(2,4,6-tribromophenolato)di(pyridine)Ni(II) complexes (20, 21) resulted in higher percent conversion than their NMIZ counterparts of the current study Co(TBP)$_2$(NMIZ)$_2$ and Ni(TBP)$_2$(NMIZ)$_2$, respectively. This observation could be explained on the basis of MS results of the previous studies, where the gaseous product was found to be mainly of ligand pyridine which does not lead to a reduction
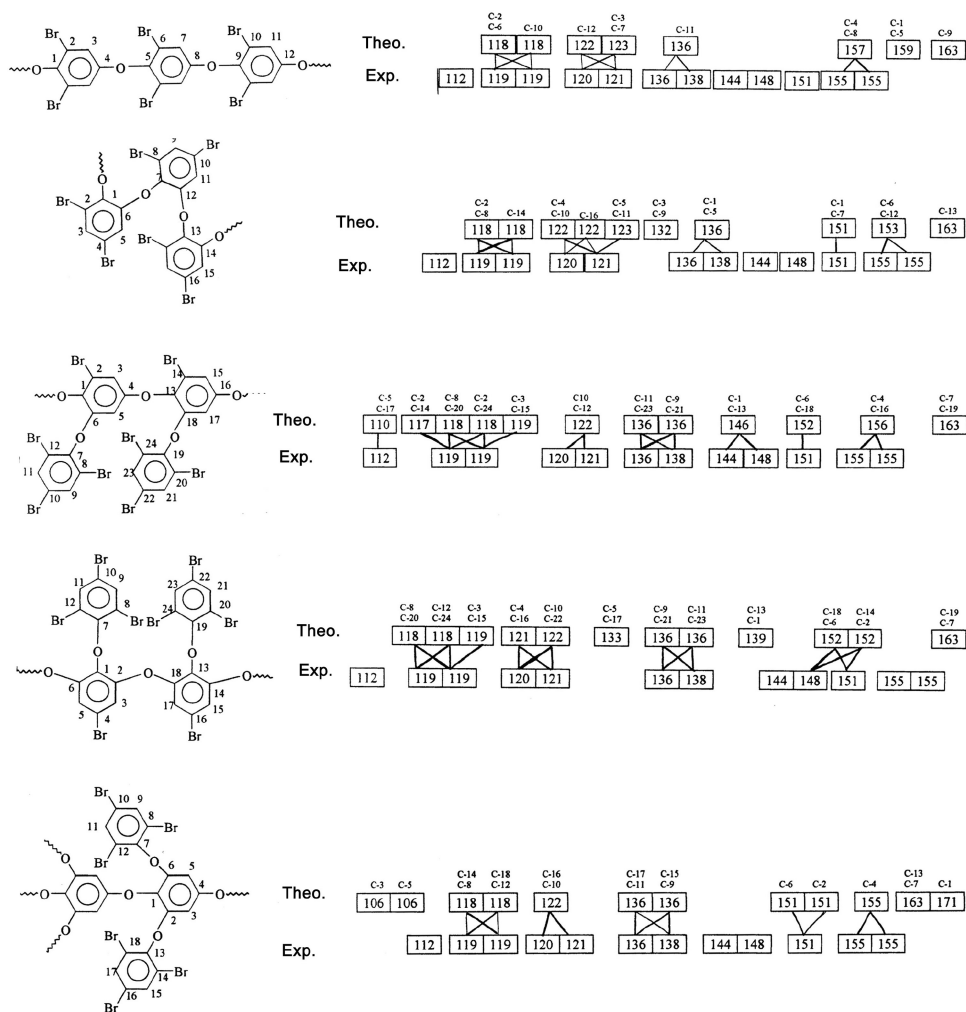

Fig. 10. ^{13}C-NMR shift data of the polymer obtained from Co(TBP)$_2$(NMIZ)$_2$ complex.

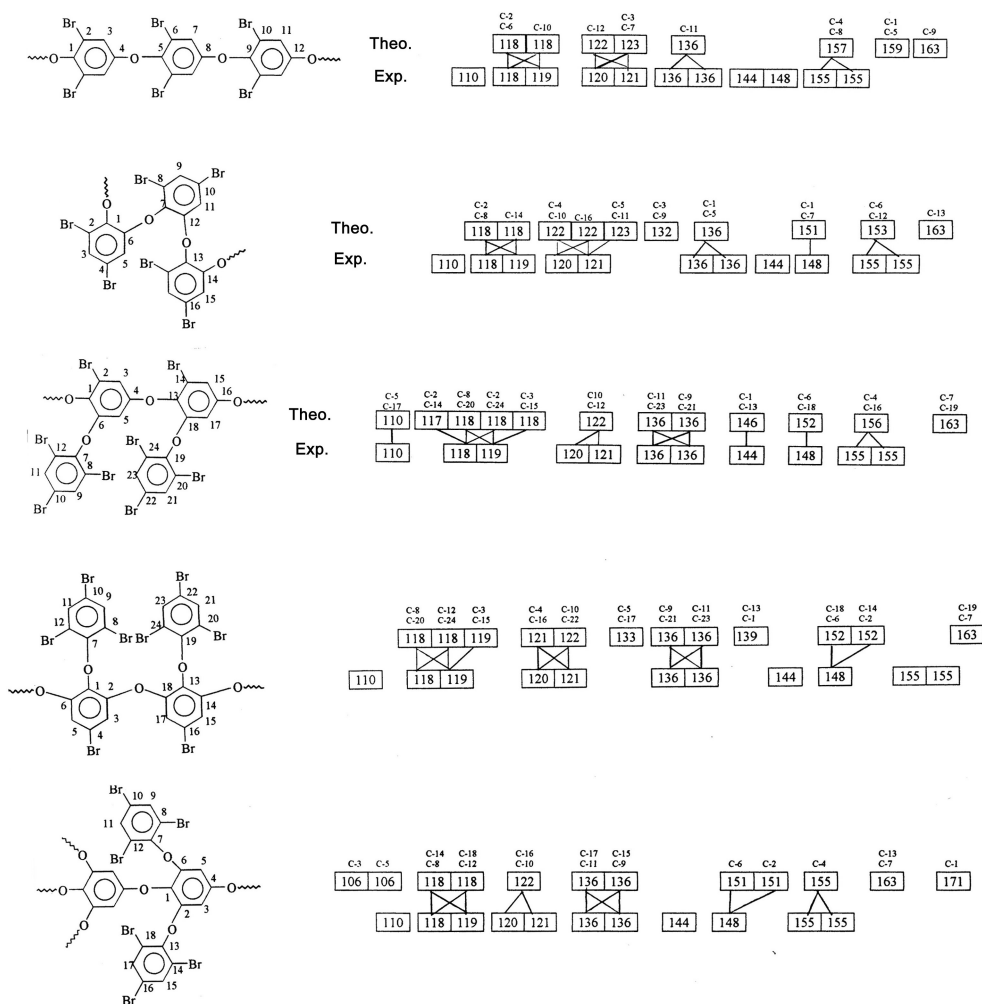**Fig. 11.** ^{13}C-NMR shift data of the polymer obtained from Ni(TBP)$_2$(NMIZ)$_2$ complex.

in the phenol content. The structural differences of the staring complexes could have an effect on this behavior also.

^{13}C-NMR decoupled spectra of the polymers obtained from complexes were displayed in Figures 8(a,b,c). The theoretical ^{13}C-NMR chemical shift data for the main five possible products were calculated by using the appropriate correlation tables (22) and binary relations between observed and calculated data for all polymers are listed in Figures 9, 10 and 11. Within the five possible structures of synthesized poly(dibromophenylene oxide)s from all complexes, ^{13}C-NMR shift data showed that the structure c (1,2 and 1,4 addition) was the most predominant one with the highest correlation of the calculated and the observed data. ^{1}H-NMR spectra of polymers obtained from decomposition of the complexes were also shown in Figures 12(a,b,c).

^{1}H-NMR spectrum of the polymers obtained from decomposition of complexes revealed that the peaks between $\delta = 7.85$–7.65 and $\delta = 7.19$–7.26 ppm were due to the fifth and third protons of 2,4-dibromo-1,6-phenylene oxide

units (1,2-addition), respectively; peaks between $\delta = 6.78$–7.1 were due to the protons of 2,6-dibromo-1,4-phenylene oxide units (1,4-addition) and the broader peaks at higher field indicated the presence of both 1,2- and 1,4-addition at the same monomeric unit. Thus, the results implied that polymerization proceeds through both 1,2-addition and 1,4-addition at equal rates for all of the synthesized polymers without regarding the type of the transition metal in the complex, leading to branched structure.

DSC thermograms of the polymers synthesized through solid state thermal decomposition of the complexes Cu(TBP)$_2$(NMIZ)$_2$, Co(TBP)$_2$(NMIZ)$_2$ and Ni(TBP)$_2$(NMIZ)$_2$ complexes revealed glass transition temperatures of 210.7, 197.7 and 189.9°C, respectively. High T$_g$ values indicated the rigidity of the synthesized polymers. Scanning electron microscopy was employed to investigate the morphology of the synthesized polymer. Micrographs (Figure 13) implied granular structure of the polymer which was different than poly(dichlorophenylene oxide) (23).

(a)

(b)

(c)
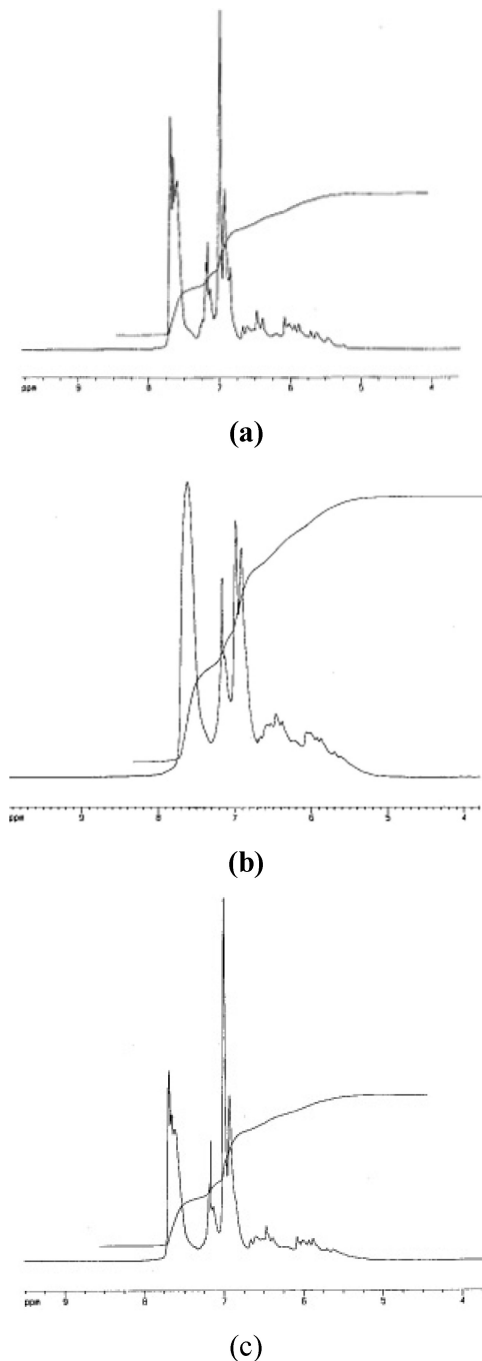
Fig. 12. ^{1}H-NMR Spectrum of the polymer obtained from the decomposition of a) Cu(TBP)$_2$(NMIZ)$_2$, b) Co(TBP)$_2$(NMIZ)$_2$ and, c) Ni(TBP)$_2$(NMIZ)$_2$.

4 Conclusions

Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)-Cu(II), Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Co(II) and Bis(2,4,6-tribromophenolato)di(N-methyl imidazole)Ni(II) complexes can be polymerized in solid state. The optimum conditions for the synthesis of poly(dibromophenylene oxide)s through thermal
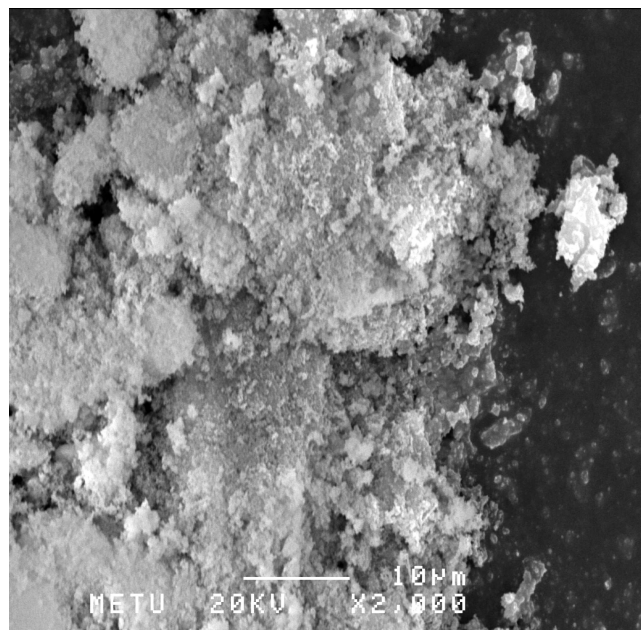
Fig. 13. SEM micrograph of the poly(dibromophenylene oxide).

decomposition of Cu(TBP)$_2$(NMIZ)$_2$, Co(TBP)$_2$(NMIZ)$_2$ and Ni(TBP)$_2$(NMIZ)$_2$ complexes were 200°C, 140°C and 210°C; revealing 30.6, 34.4, and 22.4 percent conversions at decomposition time of 3 h, respectively. Among the synthesized polymers, polymers synthesized through the decomposition of Ni(TBP)$_2$(NMIZ)$_2$ complexes yielded lowest intrinsic viscosity and percent conversion. This fact could be related with the difference in the structure of the complexes and the oxidizing power of metal. The effect of time on both percent conversion and intrinsic viscosity was also investigated. Intrinsic viscosity of the polymer synthesized via decomposition of Cu(TBP)$_2$(NMIZ)$_2$ and Co(TBP)$_2$(NMIZ)$_2$ increased slightly as the time elongated, whereas Ni(TBP)$_2$(NMIZ)$_2$ was not affected.

In this study, mass spectroscopy used as an effective tool to understand the origin of the gaseous products evolved during decomposition of the complexes and its effect on the percent conversion during polymer synthesis. Results revealed that gaseous products mainly originated from the loss of halogenated phenol, which had adverse effect on percent conversions. Extensive work has been devoted to understand the effect of by-product formation on percent conversion and intrinsic viscosities for the first time. An increase in both percent conversion and intrinsic viscosity of the polymeric products were observed beyond the melting point of the by-products which was considered to be due to ease of diffusion in solid state and it was an important factor in achieving high percent conversions. Hence, authors concluded that the thermal behavior of the by-product and the MS studies can enlighten the underlying reason of the variations at percent conversion and intrinsic viscosity values of the resultant polymeric products.

Acknowledgments

References

1. Hunter, W.H., Olson, A.O. and Daniels, E.A. (1916) *J. Am. Chem. Soc.*, 38, 1761.
2. Blanchard, H.S., Finkbeiner, H.L. and Russell, G.A. (1962) *J. Polym. Sci.*, 58, 469.
3. Carr, B. and Harrod, J.F. (1973) *J. Am. Chem. Soc.*, 95, 5707–5712.
4. Harrod, J.F., Van Gheluwe, P., Kısakürek, D. and Shaver, A. (1981) *Macromolecules*, 14, 565–570.
5. Harrod, J.F. and Shaver, A. (1982) *Macromolecules*, 15, 676–678.
6. Kısakürek, D., Binboğa, N. and Harrod, J.F. (1987) *Polymer*, 28, 1767–1771.
7. Harrod, J.F. (1969) *Can. J. Chem.*, 47, 637–647.
8. Saçak, M., Akbulut, U., Kısakürek, D., Türker, L. and Toppare, L. (1989) *J. Polym. Sci. Polym. Chem.*, 27, 1599–1608.
9. Ünal, H. İ., Sanli, O. and Kisakurek, D. (1989) *Polymer*, 30, 344–347.
10. Türker, L. and Kısakürek, D. (1988) *Brit. Polym. J.*, 20, 131–141.
11. Celik, G.B. and Kisakurek, D. (2006) *Des. Mon. Polym.*, 9(6), 663–676.
12. Celik, G.B., Sultan, W. and Kisakurek, D. (2006) e-Polymers, no. 073.
13. Şen, Ş. and Kısakürek, D. (1993) *Polymer*, 34, 4146–4149.
14. Baştürkmen, M. and Kısakürek, D. (1993) *Polymer*, 34, 625–629.
15. Şanlı, O. and Kısakürek, D. (1992) *Makromol. Chem.*, 193, 619–625.
16. Baştürkmen, M. and Kısakürek, D. (2004) *J. Macmol. Sci. Part A, Pure & Appl. Chem.*, 41, 1071–1086.
17. Camurlu, P., Yilmaz, A., Tatar, L., Kısakürek, D. and Ülkü, D. (2005) *Cryst. Res. Technol.*, 40(3), 271–276.
18. Yilmaz, A., Camurlu, P., Tatar, L., Kısakürek, D. and Ülkü, D. (2006) *Cryst. Res. Technol.*, 41, 829–835.
19. Fares, M.M., Hacaloğlu, J. and Süzer, S. (1994) *Eur. Polym. J.*, 30, 845–850.
20. Kesici, N. and Kisakurek, D. (2001) *Polym. Int.*, 50, 1061–1067.
21. Kısakürek, D. and Aslan, A. (2000) *Polymer*, 41, 5149–5155.
22. Silverstein, K.M., Bassler, G.C. and Morrill, T.T. Spectrometric Identification of Organic Compounds, 5th Ed. John Wiley & Sons: New York, 1991.
23. Çakmak, O., Baştürkmen, M. and Kısakürek, D. (2004) *Polymer*, 45, 5451–5458.