International Journal of Education and Science Research Review
Volume-2, Issue-1 February- 2015 E-ISSN 2348-6457
P-ISSN 2348-1817
www.ijesrr.org Email- editor@ijesrr.org

Synthesis & Characterization of Polyether Azomethines

Mamta Gautam
Department of Chemistry
Kisan(P.G.) College
Simbhaoli, Hapur

ABSTRACT:

The azomethine bond–CH=N– is formed during polycondensation of aromatic/aliphatic diamines with aromatic/aliphatic dialdehydes. The literature of polyazomethines is extensive. A number of researchers have tried to synthesize high molecular weight polymers but failed due to poor solubility in common organic solvents. Polyazomethines are of interest because of their high thermal stability ability to form metal chelates,(11–14) and for semiconducting properties.

Keywords: Azomethines, Benzaldehyde,

1. INTRODUCTION:

The first polyazomethines were reported by Adams and co–workers(19) in 1923. Between 1950 and 1959 Marvel and co–workers(11–13) reported a number of polyazomethiene. Suematsu and Morgan and co–workers have also reported the synthesis of some soluble, film– and fiber–forming polyazomethines.(7,20,21)

It is established that the presence of ether linkages in the polymer molecule imparts chain flexibility, lowers glass transition temperature, and enhances solubility while maintaining the desired high temperature characteristic.(22–24) There are also reports that the presence of an oxygen atom between two benzene nuclei in the repeat units of polyazomethines increases the semiconducting properties(25).

To get soluble, fusible, and semiconducting polyazomethines we have incorporated ether linkages in the main chain of azomethine polymers. This chapter reports the synthesis and characterization of six new polyazomethines with high thermal stability and semiconductivity.

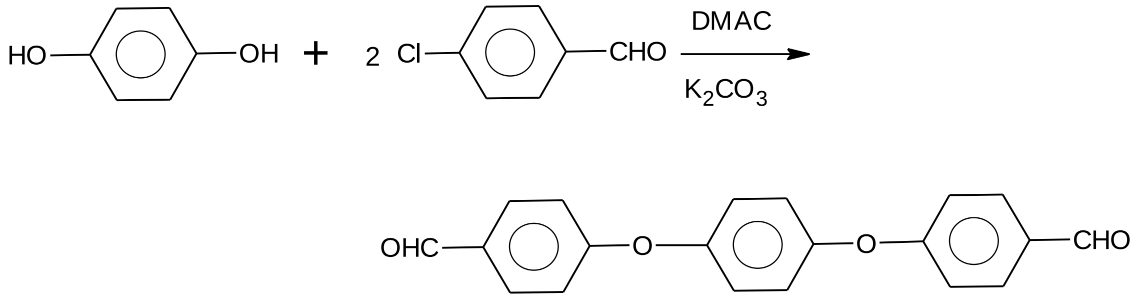
2. EXPERIMENTAL:

(i) Materials

p–Chlorobenzaldehyde (Aldrich, USA) was used as received. Hydroquinone (SD, India) was recrystalized from water. Benzidine (LOBA, India) was recrystallized from water–ethanol mixture, and decolorized by activated charcoal; mp 126°C (lit. 128°C). Diaminodiphenyl ether (Fluka, Switzerland) was recrystallized from dehydrated alcohol in the presence of activated charcoal: mp 187°C (lit. 189–191°C). Diaminodiphenyl methane (Fluka, Switzerland) was purified by recrystallization from toluene: mp 88–90°C (lit. 91–92°C). o–Aminophenol (Merck, German) and 1,6–diaminohexane (Fluka, Switzerland) were used as received. Aniline and 1,3–diaminopropane (Merck, German) were distilled prior to use. N,N–dimethyl acetamide (DMAC) was purified by distillation and dried over ahydrous $MgSO_4$.

(ii) Synthesis of 4,4|–[1,4–Phenylene bis(oxy)]bis benzaldehyde

This compound was prepared by the reaction of hydroquinone and p–chlorobenzaldehyde in DMAC in the presence of anhydrous K_2CO_3 following the procedure reported earlier(26)



The compound was characterized by IR, ^{1}H–NMR, mass spectrum, microanalysis, and HPLC technique. The yield was 90% after recrystallization from DMAC, mp: 156°C; m/z (EI): 318.0 (molecular ion and base peak): HPLC purity: 99%.

(iii) Synthesis of Model Compound

A solution of $4,4^{|}$–[1,4–phenylene bis(oxy)]bisbenzaldehyde (3.18 g, 0.01 mol) and aniline (1.86 g, 0.02 mol) in DMAC (50 mL) was stirred at room temperature for 1 h. The solvent was distilled off and dried under vacuum to give white crystalline solid. The yield was 99%, mp., 184°C; IR (KBr) 1626 cm^{-1} (C=N).

Anal. Calcd. For ($C_{32}H_{24}N_2O_2$): C–82.05%; H, 5.31%; N, 5.98%; found: C–81.72%; H, 5.25%; N, 5.84%.

(iv) Polycondensation

A typical example of the polycondensation is described.

(a) Synthesis of Polyether Azomethine

Solution. In a three–necked flask (50 mL) fitted with a stirrer and nitrogen inlet were placed benzidine [1.84 g (0.01 mol)] and dry N,N–dimethyl acetamide (25mL) containing 5% dry lithium chloride. When the solution became clear, dialdehyde [3.18 g (0.01 mol)] was added, the flask was stoppered, and the mixture was allowed to stir overnight at room temperature. Finally, the mixture was refluxed for 4 h. Sufficient quantity of water was added so as to precipitate any soluble polymer. The polymer was collected by suction filtration, washed with water, DMAC, ethanol, and ether and dried under vacuum at 80°C for 5 h.

(b) Melt. Benzidine [1.84 g (0.01 mol)] and dialdehyde [3.18 g (0.01 mol)] were placed in a 150 mL three–necked round–bottom flask equipped with a stirrer, a nitrogen inlet, and a distilling head. The temperature was raised to 250°C over a 30 min period while the by–product water was collected. The solid was removed from the flask, ground, washed with DMAC and ethanol, and dried in a vacuum oven at 80°C for 5 h.

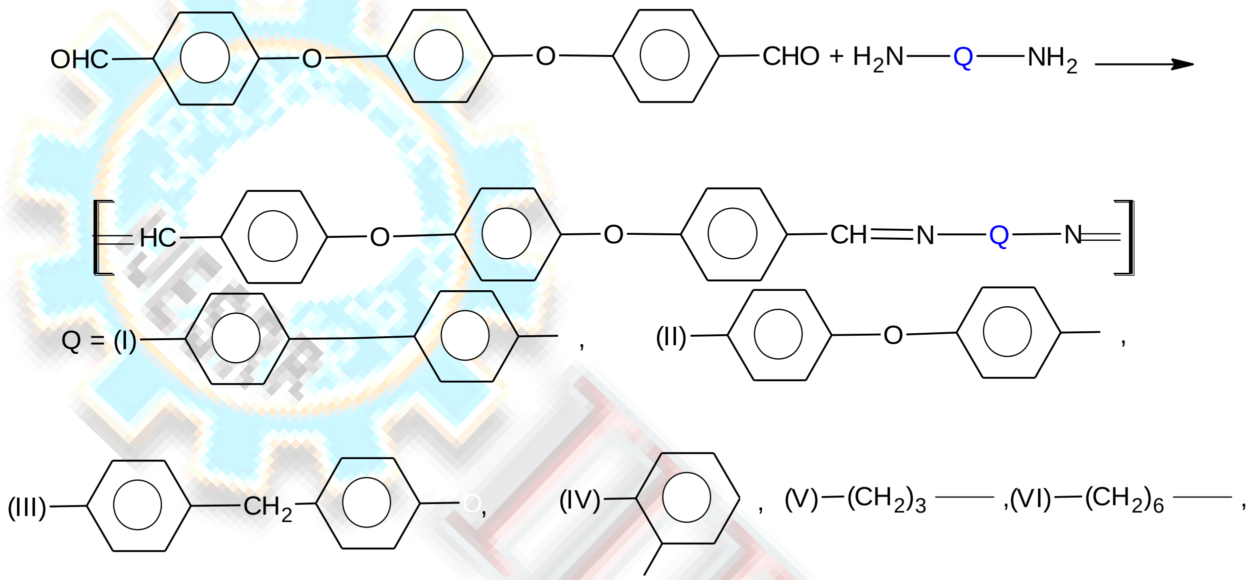
(v) Characterization

Viscosity measurements were carried out with 0.5% (w/v) polymer solutions in conc. H_2SO_4 at 30°C using a suspended level viscometer. The elements, viz. carbon, hydrogen and nitrogen were analyzed by a Heraeus Carlo Erba 1106 elemental analyzer. The density of the polymer samples was determined by an Quantachrome Micropycnometer using nitrogen gas. Infrared (IR) spectra were recorded on a Perkin–Elmer Model–577 infrared spectrophotometer with KBr pellet. X–ray diffractograms of the polymers were recorded with a Philips, Model PW 1840 x–ray diffractometer using Ni–filtered CuK$_\alpha$ radiation (40 KV, 20 ma). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done with a TA 900 series DSC 10 & TGA 51 instrument at a heating rate of 10°C/min. Electronic spectra of the polymer samples were recorded with a JASCO UVIDEC 610 spectrophotometer using sulfuric acid as solvent. Electrical conductivity measurements were done by a four–point probe d.c. technique at ambient temperature (30°C) using pressed pellets and the average of at least four individual determinations was taken.

3. RESULTS AND DISCUSSION:

(i) Polymer Synthesis and Characterization

The polycondensation of an equimolar mixture of $4,4^{|}$–[1,4–phenylene bis (oxy)]bis benzaldehyde with six different diamines were carried out by two different techniques (solution and melt) according to the following scheme:



The results of the synthesis and the physical characteristics of the polymers are summarized in Table 6.1. The polyetherazomethines (except IV) ($C_{20}H_{14}NO_2$) are insoluble in common organic solvents but all the polymers dissolve completely in concentrated H_2SO_4. The poor solubility of these polymers may be attributed to the rod–like chain structures.$^{(27)}$ The polymer IV ($C_{20}H_{14}NO_2$) is highly soluble in polar organic solvents (e.g. DMF, DMAC, DMSO, THF etc.). The high solubility of this polymer can be ascribed to the unsymmetric. 1,2–linkages in the polymer main chain which reduces the polymer close packing.

It is observed that the yield of the polymers by solution and melt method are almost quantitative. The polymers obtained by melt condensation in general show higher viscosity than the polymers obtained by solution method. Specially, in the case of IV–VI, ($C_{20}H_{14}NO_2$); ($C_{23}H_{20}N_2O_2$); ($C_{26}H_{26}N_2O_2$) very high inherent viscosity of the polymers was obtained by the melt condensation method. Probably due to the low melting temperatures of IV–VI ($C_{20}H_{14}NO_2$); ($C_{23}H_{20}N_2O_2$); ($C_{26}H_{26}N_2O_2$), the polymers melted at the reaction temperature and form a homogeneous melt and allow the chain extension to occur. Due to very high polymer melting temperature this was not possible in the case of I–III ($C_{32}H_{22}N_2O_2$); ($C_{32}H_{22}N_2O_2$); ($C_{23}H_{24}N_2O_2$). In case of solution polycondensation, the resulted polymers get separated (except IV) ($C_{20}H_{14}NO_2$) from the solvent at the early stage of polycondensation and consequently are of lower molecular weight.

The inherent viscosity values of the six polyetherazomethines in conc. H_2SO_4 are in the range of 0.45–0.74 dL/g. However, it is well known that polyazomethines undergo extensive degradation in the presence of strong protonic acid due to hydrolysis of the –CH=N– linkage$^{(16)}$. This degradation is revealed by the IR spectra of the dichloromethane extracts of polyetherazomethine–sulfuric acid solution. The spectra do not show any absorption due to the –CH=N– bond, but, match completely with the spectrum of $4,4^{|}$–[1,4–phenylene bis(oxy)]–bisbenzaldehyde. Therefore, the observed viscosities of the polyazomethines in conc. H_2SO_4 should be viewed with skeptism. It is also observed that sulfuric acid casted polymer films decolorized rapidly when immersed in water.

(ii) IR–Spectral Studies

The IR spectra of polymer I, II and III ($C_{32}H_{22}N_2O_2$); ($C_{32}H_{22}N_2O_2$); ($C_{23}H_{24}N_2O_2$) show a weak absorption at 3040 cm^{-1} for aromatic –CH, imine –CH absorption at 2860 cm^{-1}, and C=O absorption at 1690 cm^{-1} (very weak, due to terminal aldehyde group), and strong absorption at 1620 cm^{-1} for –CH=N–. The model compound prepared by the reaction of aniline and 4,4'–[1,4–phenylene bis (oxy)] bisbenzaldehyde also show similar IR absorption except the –C=O absorption. Polymer IV($C_{20}H_{14}NO_2$) show IR absorption at 1610 cm^{-1} due to –CH=N–. Polymers V and VI ($C_{23}H_{20}N_2O_2$); ($C_{26}H_{26}N_2O_2$) show similar IR patterns; a weak absorption at 3040 cm^{-1} for aromatic –CH, imine–CH absorption at 2840 cm^{-1}, aliphatic –CH absorption at 2930 cm^{-1}, and a strong absorption at 1650 cm^{-1} for –CH=N–. The elemental composition also correspond with the structure for all the polymers (Table 6.1).

The wide angle x–ray diffraction pattern of the polymers I–VI (except IV) showed sharp peaks around $2\theta = 15–30°$ indicating highly crystalline morphology. This highly crystalline nature of the polymers is due to their symmetrical rigid structure(15). The diffraction patterns of polymer I, IV and V are shown in Figure 1. The broad peak of polymer (IV) around $2\theta=15–30°$ is attributed to its amorphous nature. This is due to nonsymmetrical 1,2–linkages in the main chain polymer backbone.

(iii) Thermal Properties

The thermal behavior of the polymers was examined by TGA in both air and nitrogen atmosphere. The results of TGA, IGA, and DSC studies of the six polymers under this investigation are presented in Table 6.2.Polymers I–III ($C_{32}H_{22}N_2O_2$); ($C_{32}H_{22}N_2O_2$); ($C_{23}H_{24}N_2O_2$) are stable to thermal and thermo oxidative degradation, up to around 400°C. Thermal stability of the polymers IV–VI ($C_{20}H_{14}NO_2$); ($C_{23}H_{20}N_2O_2$); ($C_{26}H_{26}N_2O_2$) is reduced relative to polymers I–III as evidenced by the onset of thermal decomposition in the range of 350–450°C. The high thermal stability of polymers I–III is mainly due to the presence of rigid azomethine linkages(7) & symmetric 1,4–aromatic moieties in the macrochain.

Table 6.1. Synthesis and Physical Properties of Polyetherazomethines Prepared by Solution Method

Polymer	η_{inh}^{a} [Solution (Melt)] (dL/g)	Density (g/cm^3)	Colour	Microanalysis [Calculated (Found)] %			Melting point (°C)	γC=N	γC=O
				C	H	N			
I ($C_{32}H_{22}N_2O_2$)	0.45 (0.49)	1.719	Yellow	82.40 (81.72)	4.72 (4.69)	6.00 (6.11)	> 300	1620	1690
II ($C_{32}H_{22}N_2O_2$)	0.47 (0.50)	1.635	Light yellow	79.66 (79.42)	4.56 (4.52)	5.80 (5.73)	>300	1620	1690
III ($C_{23}H_{24}N_2O_2$)	0.53 (0.59)	1.667	Light yellow	82.50 (82.0)	5.00 (4.98)	5.83 (5.90)	> 800	1620	1690
IV ($C_{20}H_{14}NO_2$)	0.52 (0.63)	1.120	Light yellow	80.00 (79.84)	4.66 (4.59)	4.66 (4.56)	140	1616	–
V ($C_{23}H_{20}N_2O_2$)	0.59 (0.72)	1.249	White	77.52 (77.14)	5.61 (5.59)	7.86 (7.92)	235–240	1650	–
VI ($C_{26}H_{26}N_2O_2$)	0.54 (0.74)	1.235	White	78.89 (77.87)	6.53 (6.54)	7.03 (7.12)	228–235	1650	–

[a] Measured in 97% H_2SO_4 solution (0.5 g/dL) at 30°C

The low thermal stability of IV,V, and VI are due to unsymmetric 1,2−aromatic and aliphatic moieties in the polymer main chain respectively. Isothermal gravimetric analysis of polymers I−VI was carried out at 300°C in air. Polymers I−VI showed only 4.6−13.2% weight loss after 20 h of heating. The TGA and IGA results show that the polymers have little or no effect of atmosphere on thermal stability. Polymers V and VI are thermooxydatively less stable in comparison to I–IV. This may be due to presence of oxidizable $–CH_2–$ linkages in the polymer main chain.

DSC curves also supported the results of TG studies. DSC curves of polymers II, III, V, and VI show sharp endotherms (Table 6.2), which can be attributed to the polymer melting temperature. The sharp melting endotherms supported the crystalline morphology of these polymers. The melting point of the polymers V and VI determined by electro− thermal capillary melting point apparatus matches well with the DSC melting temperature. The broad exotherms are due to the thermally induced cross−linking of the azomethine (–CH=N–) double bonds.(28) The broadening of the IR absorption band for the cured samples of polyetherazomethines in the range of 1620–1650 cm^{-1} indicates crosslinking.

(iv) Electrical Properties

The electric conductivities of polyetherazomethines I−VI range from 10^{-11}–10^{-16} S/cm at 30°C (Table 6.3). The polymer I, prepared from benzidine as diamine had somewhat higher electrical conductivity. Viz, 2.8×10^{-11} S/cm. The electrical conductivity of polymer IV prepared from o−phenylene diamine is the lowest; 8.3×10^{-16} S/cm. It is reported that for semiconducting polymers electrical conductivity increases with increase in the chain length of the conjugated system or the repeat unit of the polymer chain in the absence of steric effect(16,29). Polymer IV has low conductivity due to this effect. Although, in the case of polymer III the conjugated units are insulated by an insulating bridge $–CH_2–$, the electrical conductivity of III is comparable to I and II. The electrical conductivity of V and VI are significantly lower than the polymers I and II. The low electrical conductivity of polymers V and VI may be due to the presence of longer insulating bridges. $–(CH_2)_3–$ and $–(CH_2)_6–$, respectively. Thus, the role of nonconjugating bridges on electrical conductivity is not very clear. Doping with iodine as electron acceptor was done until the polymers were saturated with iodine. As doping proceeded, the colour of each polymer changed to dark brown. The doping occurs only at the surface as can be seen by breaking the pellet(17). IR spectra of the doped polymer show a significant disappearance of aromatic and imine –CH peaks and a broadening of –CH=N– absorption, which is due to the oxidation of the double bond by I_2.(16) After doping with iodine, the electrical conductivity of the polyetherazomethines increases significantly. Although these polymers in virgin state are insulators, they can be converted into semiconductors by doping with iodine. The polyetherazomethines prepared by melt condensation method shows a somewhat lower electrical conductivity than the same polymers prepared by the solution method. This observation is quite unusual and may be due to the difficulty of preparing a compact pellet. The polymers prepared by the melt method are hard and slippery and not amenable to be broken into a fine powder required for the preparation of compact pellet.(18–22)

The electronic spectra of the undoped polymers were compared with the model compound to get more detailed information about the electronic state of the polymers. As shown in Table 6.3 the spectra of polymers I, II and III in sulfuric acid showed large bathochromic shift of the π–π* absorption band due to –CH=N– absorption bands from the absorption maximum of model compound (max 376 nm, Table 6.3). This indicates that a large number of recurring units take part in the conujugation(23–28). The lower bathochromic shift of the π–π* absorption due to the –CH=N– bond in case of polymer III compared to polymers I and II is due to the presence of insulating $–CH_2–$ in the polymer main chain. This observation is not in consonance with comparable electrical conductivity of III with I and II. Polymer II, where all the benzene nuclei is separated by oxygen atom shows a lower bathochromic.(30–35) shift of the $\pi-\pi^*$ absorption due to –CH=N– bonds compared to polymer–I. This indicates that polymer–II is less conjugated than polymer–I.

Thus, this observation does not support the view that the presence of an oxygen atom in between two benzene rings increases the semiconducting properties of polyazomethines(36–38). The electrical conductivity of the undoped and doped polyetherazomethines, therefore, is related to the presence of delocalized– electrons.

(v) CONCLUSION

Fusible, thermo and thermooxidative stable polyetherazomethines have been prepared. Polyetherazomethines I, II, and III can be considered as novel high–temperature resistant semiconductor. Further investigation on the electrical conductivity of polyetherazomethines are required to better understand the electrical properties of this class of polymers.

Table 6.2: Thermal Stability of Polyetherazomethines Prepared by Solution Method

THERMAL STABILITY*

Polymer Code	**Initial Decompo. Temp. (°C)**		**10% Weight Loss Temperature (°C)**		**Char Residue Wt % at 700°C**		**Isothermal Stability Weight Loss (%) at 300°C for 20 h in Air**	**DSC Melt Endotherm (°C)**
	Nitrogen	**Air**	**Nitrogen**	**Air**	**Nitrogen**	**Air**		
I $(C_{32}H_{22}N_2O_2)$	454	450	493	490	60	54	4.6	–
II $(C_{32}H_{22}N_2O_2)$	425	422	462	461	57	52	4.2	405.9
III $(C_{23}H_{24}N_2O_2)$	422	420	462	460	53	49	4.8	385.7
IV $(C_{20}H_{14}NO_2)$	400	393	512	450	30	28	6.0	–
V $(C_{23}H_{20}N_2O_2)$	353	342	422	372	32	17	8.6	236.6
VI $(C_{26}H_{26}N_2O_2)$	355	338	438	368	22	16	13.2	228.6

*Determined by TGA, Heating rate, 10°C/min.

Table 6.3: Electric Conductivity (σ) of Polyetherazomethines Prepared by Solution Method

Polymer	**Affinity[a] Towards I_2, 24 h (wt %)**	**Electric Conductivity[b] (S/cm)**			**$\lambda_{maximum}$ (nm)[c]**
		Solution		**Melt**	
		Undoped	**I_2 doped**	**Undoped**	
I $(C_{32}H_{22}N_2O_2)$	22.6	2.8×10^{-11}	7.7×10^{-6}	$5. 9 \times 10^{-12}$	416
II $(C_{32}H_{22}N_2O_2)$	18.9	7.2×10^{-12}	2.1×10^{-6}	8.1×10^{-13}	398
III $(C_{23}H_{24}N_2O_2)$	16.8	4.5×10^{-12}	3.5×10^{-6}	8.4×10^{-13}	385
IV $(C_{20}H_{14}NO_2)$	14.2	8.3×10^{-16}	1.2×10^{-9}	7.2×10^{-16}	282
V $(C_{23}H_{20}N_2O_2)$	14.6	4.2×10^{-13}	3.2×10^{-7}	2.1×10^{-13}	342
VI $(C_{26}H_{26}N_2O_2)$	13.8	5.7×10^{-14}	4.1×10^{-8}	9.1×10^{-15}	334
Model	–	–	–	–	376

[a] Iodine content was calculated from the weight increase.

[b] Measured by a four–probe, d.c. method at 30°C.

[c] Measured in concentrated sulfuric acid (concn. 10^{-5}M).

REFERENCES

1. G.F.D'Alelio, Encycl. Polym. Sci. Technol., 10, 659 (1969).
2. A.D.Delman, A.A.Stein, and B.B.Simms, J. Macromol. Sci. Chem., A1, 147 (1967).
3. R.J.Cotter and M.Matzner, Org. Chem. (N.Y.), 13B (1), 1 (1972).
4. H.A.Goodwin & J.C.Bailer, Jr., J.Am.Chem. Soc. 83, 2467 (1961).
5. S.Banerjee, S.K.Palit, and S.Maiti, J.Polym. Mater., 9, 219 (1992).
6. P.W.Morgan, T.C.Pletcher, and S.L.Kwolek, Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem., 24(2), 470 (1983).
7. K.Suematsu, K.Nakamura, and J.Takada, Coll. Polym. Sci., 261, 470 (1983).
8. K.Suematsu, K.Nakamura, and J.Takada, Polym, J., 15, 71 (1983).
9. C.J.Yang and S.A.Jenekhe, Chem. Mater., 3, 878 (1991).
10. Y.Saegusa, K.Sekiba, and S.Nakamura, Kenkya Hokoku, Asahi Garasu Zaidan, 56, 139 (1990).
11. C.S.Marvel and W.H.Hill, J. Am. Chem. Soc., 72, 4891 (1950).
12. C.S.Marval and N.Tarkoy, J.Am. Chem. Soc., 80, 832 (1958).
13. C.S.Marval & P.V.Bonsignore, J.Am.Chem. Soc. 81, 2668 (1959).
14. W.E.Rudzinski, S.R.Guthrie, and P.E.Cassidy, J.Polym. Sci. Part A: Polym. Chem., 26, 1677 (1988).
15. Y.Saegusa, K.Sekiba and S.Nakamura, J.Polym. Sci. Part A: Polym. Chem., 28, 3647 (1990).
16. M.S.Patel and S.R.Patel, J. Polym. Sci. Part A: Polym. Chem., 20, 1985 (1982).
17. K.B.Al–Jumah, K.B.Wagener, and T.E.Hogen Esch, Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem. 30(2), 173 (1989).
18. Y.Saegusa, T.Takashima, and S.Nakamura, J. Polym. Sci; Part A: Polym. Chem; 30, 1375 (1992).
19. R.Adams, R.E.Bullock, and W.C.Wilson, J. Am. Chem. Soc., 45, 521 (1923).
20. P.W.Morgan, S.L.Kwolek, and T.C.Pletcher, Macromolecules, 20, 729 (1987).
21. P.W.Wojtkonski, Macromolecules, 20, 740 (1987).
22. P.M.Hergenrother, N.T. Wakelyn, and S.J.Havens, J. Polym. Sci. Part A: Polym. Chem. 25, 1093 (1987).
23. S.Maiti and B.K.Mandal, Prog. Polym. Sci., 12, 111 (1986).
24. A.A.Kulkov, S.N.Salazkin, G.L.Sonimskii, A.A.Askadskii, K.A.Bychke, S.V. Vinogradov and V.V.Korshak, Vysokomolek. Soedin Ser. A, 16, 1543 (1947).
25. A.V.Toopchiev, V.V.Korshak, U.A.Popv, and L.D.Rosenstein, J. Polym. Sci. C. 4, 1305 (1964).
26. G.W.Yeager and D.N.Schissel, Synthesis, 63 (1991).
27. B.Milland, C.Strazielle, and G.Well, Polymer. 21, 639 (1980).
28. J.A.Mikroyannidis, J.Polym. Sci; Part A: Polym. Chem; 27, 3465 (1989).
29. G.Manecke and J.Danhaeuser, Macromol. Chem. 84, 238 (1965).
30. Y.Saegusa, T.Koshikawa and S.Nakamura, J.Polym. Sci. Part A, Poly. Chem. 30, 1373
31. A.Pron and P.Rannou, Prog. Polym. Sci; 27, 135 (2002).
32. S.Bhadra, D.Khastgir, N.K.Singha & J.H.Lee, Prog. Polym. Sci; 34, 783 (2009).
33. G.Sotzing & K.Lee, Macromolecules 35, 7281 (2002).
34. L.Miguel & A.J.Matzger, Macromolecules 40, 9233 (2007).
35. N.Jaballah, M.Chemli, K.Hriz, J.Fave, M.Jovini & M.Majdoub, Eur. Polym. J; 47, 78 (2011).
36. K.Oyaizu, T.Iwaski, Y.Tsukahara & E.Tsuchida, Macromolecules, 37, 1257 (2004).
37. M.Morimoto, K.Tamsura, K.Nagai and E.Yahina, J. Polym. Sci; Pt(A) Polym. Chem; 48, 1383–1390 (2010).
38. W.Lu, J.Kuwubara, T.Iijima, H.Higashimura, H.Hayashi and T.Kanbara, Macromolecules 45, 4128 (2012).