SYNTHESIS, CHARACTERIZATION, THERMAL PROPERTIES AND ANTIMICROBIAL ACTIVITY OF ACRYLIC COPOLYMERS DERIVED FROM 2,4-DICHLOROPHENYL ACRYLATE

ANKIT K. PATEL, RAJESH J. PATEL, KIRIT H. PATEL AND RAJNI M. PATEL

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India

(Received: September 2, 2008 - Accepted: October 28, 2008)

ABSTRACT

Copolymer of monomer 2,4-dichlorophenylacrylate (2,4-DCPA) and methylmethacrylate (MMA) were synthesized with different monomer feed ratio using dimethylformamide (DMF) as a solvent and 2,2'-azobisisobutyronitrile (AIBN) as an initiator at 70°C. The copolymers were characterized by IR-Spectroscopy and copolymer composition was determined with UV-Spectroscopy. The linearization method of Fineman Ross (F-R) and Kelen Tudos (K-T) were used to obtain the monomer reactivity ratios. Thermal analyses of polymer were carried out in nitrogen atmosphere thermal gravimetric analyses (TGA) and differential thermal analyses (DTA). The molecular weight and intrinsic viscosity were determined by vapor pressure osmometry (VPO). The homo and copolymers were tested for their antimicrobial properties against selected microorganisms.

Key words: Copolymer / Thermal Analysis / Reactivity Ratio / Antimicrobial Activity

INTRODUCTION

Copolymer is the most successful and powerful method for effecting systematic change in polymer [1]. Phenyl acrylate polymers are relatively newly developed materials compared to the commercial polymer such as vinyls. Acrylate is considered as reactive monomers primarily because of the presence of aromatic ring [2]. Choudhary Veena and coworkers [3-5] prepared copolymer of methyl methacrylate (MMA) with a variety of vinyl monomers. Strum [6] reported about thirty eight ester useful as commercial bactericides and fungicides. Plunder and coworkers [7] synthesized acrylics ester, useful as biocides by reacting pentachloro phenol, *p*-chloro-*m*-cresol, *o*-phenyl phenol with acryloyl chlorides. Patel and coworkers [8,9] prepared copolymer from 2,4-dichlorophenyl methacrylate with various vinyl monomers and reported that these polymer are useful as micro biocides are thermally stable up to 250°C. Ibrahim Erol [10, 11] prepared new methacrylate monomer and their derivatives and copolymerized these monomers with various vinyl monomers. Bozkurt and Karadedeli [12] prepared copolymers of 4(5)-vinylimidazole and ethylene glycol methacrylate phosphate. Vijayanand and coworkers [13] prepared novel methacrylic monomer, 4-nitro-3-methylphenyl methacrylate (NMPM) by reacting 4-nitro-3-methylphenol with methacryloyl chloride in the presence of triethylamine as catalyst. Senthilkumar and coworkers [14,15] prepared new methacrylate monomer and copolymerized it with different feed ratio of styrene/ methyl acrylate/ *N*-vinyl pyrrolidone. Reactivity ratio was calculated by applying conventional linearization method of F-R and K-T. These authors tested biological activity of polymers and reported that these polymers show good biological activity.

The present work deals with the synthesis and characterization of monomer, homopolymer and copolymers. The copolymer composition was determined by UV spectroscopy. Reactivity ratios were determined using F-R and K-T methods. The molecular weight and intrinsic viscosity were determined by VPO. Thermal stability of the polymers was also studied. Biological activity of the homo and copolymers were carried out against selected microorganism like bacteria, fungi and yeast.

EXPREMENTAL

Materials:

Acrylic acid (Chiti chem. Baroda), Benzoyl chloride (Chiti chem. Baroda), Hydroquinone (S.D. fine chem.), 2,2'-azobisisobutyronitrile (AIBN, Aldrich), 2,4-dichlorophenol (S.D. fine chem.), were analytical grade reagent (i.e. 98% pure) and used without further purification. Fractionally distillation solvent was used in the reactions.

Synthesis of Acryloyl chloride

Acryloyl chloride was prepared according to the process reported in the literature [16].

Synthesis of 2,4-dichlorophenyl acrylate (2,4-DCPA).

To a one liter three necked flask equipped with stirrer, thermometer and guard tube, absolute alcohol (200 mL) and NaOH (0.1 mole) were added and the contents were stirred until all the NaOH dissolved. To this, 2,4-dichloro phenol (0.1 mole) was added. The reaction mixture was heated at 60 °C for 30

minutes with stirring, cooled to room temperature and then to 0-5 °C. Freshly prepared acryloyl chloride (0.11 moles) was added drop wise within 60 minutes to the cooled reaction mixture. The temperature was maintained around 0-5 °C during the addition. After completion of addition, reaction mixture was stirred for 90 minutes and it was poured into crushed ice water mixture where a light brown color liquid product settled down. It was extracted with ether. The ether layer was separated out and evaporated. The liquid monomer obtained after evaporation of ether was dried over anhydride calcium chloride in vacuum desiccators. The yield was 83%.

IR of 2,4-DCPA (cm⁻¹): 3015(-CH stretching vibration of the aromatic ring), 2978(ν_{CH_3}), 1756($\nu_{\text{C=O}}$) [17], 1640($\nu_{\text{C=C}}$), 1230(asymmetric $\nu_{\text{C-O-C}}$), 1150(symmetrical $\nu_{\text{C-O-C}}$), 890(-CH bending mode of vinyl group), 730 (rocking mode of vinyl group), 667 ($\nu_{\text{C-Cl}}$) [18]. The two absorption bands at 1593 and 1480 cm⁻¹ may be assigned as the characteristic absorption of *o*-substituted phenyl ring [19, 20]. Figure 1(a) shows the IR spectrum of monomer 2,4-DCPA, and Figure 1(b) shows ¹H-NMR spectrum of monomer 2,4-DCPA.

Figure 1(a): FT-IR spectrum of monomer 2,4-DCPA.

Figure 1(b): ^1H -NMR spectrum of monomer 2,4-DCPA.

Copolymerization:

Copolymers of 2,4-DCPA with MMA having different feed composition were synthesized by free radical polymerization in DMF using AIBN as a free radical initiator. The feed composition of monomer and comonomer are giving in Table I. Appropriate quantities of monomer, comonomer, DMF (10mL) and AIBN (0.5% w/w) based on total monomers were taken in a polymerization tube equipped with reflux condenser. The reaction mixture was heated at 70°C for 5 hrs with stirring. It was then cooled to room temperature and the resulting polymer solution was slowly poured in a large volume of methanol with stirring, where the polymer precipitated out. It was filtered and washed with methanol. Solid polymer were purified by repeated precipitation by methanol from solution in DMF and finally dried. Reaction Scheme (Figure-2) show the step leading to the formation of homopolymer of 2,4-DCPA (Poly(2,4-DCPA)), MMA (Poly(MMA)) and its copolymers (Poly(2,4-DCPA-co-MMA)).

Table I: Copolymer composition and reactivity ratios of copolymers of 2,4-DCPA and MMA.

Sample Code No.	2,4-DCPA $[M_1]$ Mole	MMA $[M_2]$ Mole	% Conversion	Composition of P(2,4-DCPA) in copolymer $[m_1]$	X	Y	F	G	ξ	η
2	0.2	0.8	7.65	0.267	0.25	0.364	0.172	-0.437	0.137	-0.347
3	0.4	0.6	9.18	0.458	0.67	0.845	0.531	-0.123	0.328	-0.076
4	0.5	0.5	8.20	0.542	1.0	1.183	0.845	0.155	0.437	0.080
5	0.6	0.4	8.68	0.584	1.5	1.404	1.603	0.432	0.596	0.161
6	0.8	0.2	9.20	0.730	4.0	2.704	5.917	2.521	0.845	0.360

Where, $m_2 = 1 - m_1$; $X = M_1/M_2$; $Y = m_1/m_2$; $F = X^2/Y$; $G = X(Y - 1/Y)$; $\xi = F/\alpha + F$; $\eta = G/\alpha + F$ and $\alpha = [F_M \cdot F_m]^{1/2}$

Characterization of polymers:

NICOLET 400D FT-IR Spectrophotometer was used to record the spectrum of monomer, homopolymer and copolymer on solid KBr pellets. A Simadzu-160 recording UV-Visible spectrophotometer was used to determine copolymer composition and reactivity ratio. KNAUR (Germany) Vapor Pressure Osmometer (VPO) was used to determine the number average molecular weight of homo as well as copolymers. TA instrument (U.S.A)-2960 thermo gravimetric analyzer was used to perform TGA and DTA at a heating rate of 10°C/min in nitrogen atmosphere.

Figure 2: Reaction Scheme Synthesis of (a) poly(2,4-DCPA), (b) poly(2,4-DCPA-Co-MMA) (c) poly(MMA).

Antimicrobial Activity:

The synthesized homo- and copolymers were tested against different microorganism that's commonly employed for biodegradability tests. Bacterial strains (*Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus*), fungi (*Aspergillus niger*, *Sporotrichum pulverulentum*, and *Trichoderma lignorum*), and yeast (*Candida utilis*, *Saccharomyces cerevisiae*, and *Pichia stipitis*) were grown in Nutrient broth (N-broth) and Subourand's dextrose broth and YEPD (Yeast Extract Peptone Dextrose) media, respectively, with or without indicated polymers.

(a) Bacterial Cultivations

5% (v/v) inoculums of bacterial culture was used to inoculated 100 mL N-broth solution [control (without polymer)] and test media (100 mL N-broth + 50 mg polymer) and incubated on rotary shaker (200 rpm) at room temperature. 0.5 mL liquids were withdrawn at specified time intervals (20-48 h) from test media. After suitable dilution with distilled water, absorbance was measured at 660 nm and calculated as absorbance per mL (i.e. growth). The method is based on the principle that as the growth proceeds, cell number increases which leads to increase in absorbance of medium. The percentage inhibition for bacteria was calculated by the following formula:

$$\text{Percentage inhibition} = \frac{100(X-Y)}{X}$$

Where X= absorbance of bacterial suspension in control set
Y= absorbance of bacterial suspension in test set.

(b) Fungal Cultivation

Since fungal culture shows filamentous growth, optical method can not used to monitor the growth, therefore gravimetric analysis was carried out to determine dry cell mass. 10% (v/v) inoculum was added to the sterile control medium (without polymer) and test medium (100 mL control medium + 50 mg polymer). Flasks were incubated at room temperature on rotary shaker (200 rpm) for 40 hours. Content of flasks were filtered using cheesecloth and cell pellets were dried to constant weight. The percentage inhibition for fungi was calculated after 7 days using the following formula:

$$\text{Percentage inhibition} = \frac{100(X-Y)}{X}$$

Where X= Weight of dry fungal cell mass in control set
Y= Weight of dry fungal cell mass in test set.

(c) Yeast Cultivation

5% (v/v) inoculums of yeast culture was added to the 100 mL of sterile control medium (without polymer) and test medium (100 mL control medium + 50 mg polymer) and incubated on rotary shaker (200 rpm) at room temperature. Sample contents were withdrawn at specified time intervals (24 and 48 h) from test media. After suitable dilution with distilled water absorbance was measured at 660 nm and calculated as absorbance per mL (i.e. growth). The percentage inhibition for yeast was calculated by the following formula:

$$\text{Percentage inhibition} = \frac{100(X-Y)}{X}$$

Where X= absorbance of yeast suspension in control set
Y= absorbance of yeast suspension in test set.

RESULTS AND DISCUSSION

The Copolymerization of 2,4-DCPA with MMA in DMF solution was studied in wide composition interval with mole fraction of 2,4-DCPA ranges from 0.2 to 0.8 in the feed. The reaction time was selected to give conversion less than 10% weight to satisfy the differential copolymerization equation for calculation of reactivity ratio.

The IR-spectra of the copolymers are shown Figure-3. The two bands at 2998 cm^{-1} and 2956 cm^{-1} those that appear in all polymers are due to C-H stretching mode of alkyl group. The C-H stretching vibration of aromatic ring is assigned to a peak around 3022 cm^{-1} . The absorptions at 1390 cm^{-1} and 1475 cm^{-1} may be traced to the plane bending vibration of methyl (symmetric methyl bending) and methylene (bending of CH_2) groups. The compounds show the characteristic strong absorption due to C=O stretching of ester groups. In the copolymers two C=O stretching vibration are observed at 1765 cm^{-1} and 1725 cm^{-1} . From a comparison of spectra of (2,4-DCPA) and poly MMA with those 1765 cm^{-1} peak may be assigned to the C=O stretching of the 2,4-DCPA moiety of the copolymers and the 1728 cm^{-1} peak may be attributed to the same in the MMA moiety. The medium strong absorption in the range 1215-1246 cm^{-1} may have contribution from C-O-C stretching vibrations of the ester group. The band at 868 cm^{-1} is due to the $-\text{CH}_2-$ rocking mode of the methylene chain. The prominent sharp band at 670 cm^{-1} is attributed to C-Cl stretching [21].

The NMR signal at around 7.6 δ (Fig.-1(b)) is due to the aromatic proton No.-3 and the peak of 7.2 δ may be due to the aromatic protons No.- 1 and 2. The NMR signal due to vinylic protons appears in the 6.0 to 6.6 δ .

Copolymer Composition and Reactivity Ratio:

The average composition of each copolymer sample was determined from the corresponding UV-Spectrum. The composition of each monomer in the polymer was obtained from measurement of absorption at $\lambda_{\text{max}} = 272$ nm which is the characteristic λ_{max} for 2,4-DCPA. From monomer feed ratio and copolymer composition, the reactivity ratio of 2,4-DCPA and MMA were determined using F-R method [22] and K-T [23] method (Fig. 4 and Fig. 5 respectively).

Molecular weights and Viscosity Measurement:

The number average molecular weights of copolymers were determined by VPO using DMF as a solvent at 90°C. The value of number average molecular weight and intrinsic viscosity varies between 5382-7923 g/mol and 0.011-0.021 dL/gm respectively. From these data (Table-2) it is concluded that as the 2,4-DCPA content increases in the copolymer the molecular weight viscosity change randomly (i.e. increases or decreases).

Figure 3: FT-IR spectra of poly(2,4-DCPA) (1), poly(MMA) (7) and poly(2,4-DCPS-co-MMA) (2-6).

Figure 4: F-R plot for poly(2,4-DCPA-co-MMA).

Figure 5: K-T plot for poly(2,4-DCPA-co-MMA).

Table II: VPO and viscosity data for poly(2,4-DCPA), poly(MMA) and poly(2,4-DCPA-co-MMA).

Sample Code No.	Mn (g.mol ⁻¹)	Intrinsic Viscosity $[\eta]$ (dL.g ⁻¹)
1	7923	0.021
2	5382	0.011
3	5781	0.012
4	5945	0.013
5	6405	0.014
6	6800	0.016
7	6968	0.016

Thermal Analysis:

The data from TGA of homo and copolymers are presented in Table-3. The data clearly indicated that all polymers undergo single step decomposition except the 2,4-DCPA. Activation energy (E_a) and integral procedure decomposition temperature (IPDT) were determined by Broido's method [24] and Doyle's method [25]. Thermal studies showed that the polymers undergo decomposition in the range of 191- 440°C. The activation energy (E_a) lies in the range of 61-75 K.J. mol⁻¹.

The result of DTA of homo and copolymers are shown in Table-4. The activation energy for thermal degradation determine by Reich's method [26] of polymers ranged from 60- 76 K.J.mol⁻¹.

Antimicrobial Activity:

The microbial screening of homo and copolymer of 2,4-DCPA and MMA were investigated. The obtain results are presented in Fig. 6, 7, and 8. All the polymers showed almost similar antimicrobial properties against bacteria, fungi, and yeast. Poly(2,4-DCPA) allows 50% growth for bacterial poly(MMA) allows 92% growth for bacterial whereas its copolymer favor 68-86% growth. Fungi shows 45% growth for poly(2,4-DCPA), 91% growth for poly(MMA) and 65-87% for copolymers. Yeast shows 43% growth for poly(2,4-DCPA), 75% growth for poly(MMA) and 57-73% growth for copolymers.

All copolymers system imparts almost similar antimicrobial properties against bacteria, fungi and yeast. It was observed that polymers prepared using 2,4-DCPA showed strong inhibitory effect towards the microorganisms tested. As the 2,4-DCPA content increases in the copolymer, the effectiveness of the copolymers to inhibit the growth of microorganism increases as expected.

Table III: TGA data for homo- and copolymers of 2,4-DCPA with MMA.

Sample Code No.	% Weight loss at various temperature (°C)					Decomposition Temperature Range (°C)	Tmax ^a (°C)	T50 ^b (°C)	IPDT ^c (°C)	Activation Energy ^d (E _a) (K.J.mol ⁻¹)
	200	300	400	500	600					
1	1	6	79	87	92	191-340 341-424	389	383	403	75
2	5	11	97	99	-	274-408	358	351	355	68
3	12	18	92	95	98	214-410	373	364	385	72
4	0	1	55	81	85	307-440	398	396	402	63
5	2	26	92	-	-	241-417	366	351	378	61

^a Temperature for maximum rate of decomposition^b Temperature for 50% weight loss^c Integral procedural decomposition temperature^d By Broido's method**Table IV:** DTA data for homo- and copolymers of 2,4-DCPA with MMA

Sample Code No.	T ₁ ^a (°C)	T ₂ ^b (°C)	T _b ^c (°C)	Activation Energy ^d (E _a) (K.J.mol ⁻¹)	Reaction Order
1	385	440	412	76.44	1
2	361	482	402	66.52	1
3	380	468	399	69.77	1
4	311	402	351	60.81	1
5	295	380	322	59.80	1
	382	452	423	28.09	1

^a Starting Temperature of DTA trace^b Ending Temperature of DTA trace^c Peak maxima Temperature of DTA trace^d Activation Energy by Reich's method **Figure 6:** Effect of poly(2,4-DCPA) (1), poly(MMA) (7) and poly(2,4-DCPS-co-MMA) (2-6) on growth (%) of bacteria. **Figure 7:** Effect of poly(2,4-DCPA) (1), poly(MMA) (7) and poly(2,4-DCPS-co-MMA) (2-6) on growth (%) of fungi.

Figure 8: Effect of poly(2,4-DCPA) (1), poly(MMA) (7) and poly(2,4-DCPS-co-MMA) (2-6) on growth (%) of yeast.

CONCLUSION

The homo and copolymers of 2,4-DCPA and MMA having various composition were synthesized by solution polymerization. The monomer and polymers were characterized by spectroscopic methods. Thermal analysis show that all copolymers of 2,4-DCPA undergo single step decomposition and homo polymers decomposition in a double step. We can observe that polymers containing chlorine exhibit strong antimicrobial activity. In the co-polymers we have found that as the 2,4-DCPA content in polymer increases i.e. the amount of chlorine increases, the polymer inhibits more the growth of the microorganism. 2,4-dichloro phenol (2,4-DP), a well known biocide [27] has been anchored to a polymer by copolymerizing 2,4-dichloro phenyl acrylate (2,4-DCPA) with other vinyl monomers.

REFERENCES

1. D. A. Tirrell, M. H. Tirrell, N. M. Bikalws, C. G. Overberger and G. Menges, *Encyclopedia of Polymers Sciences and Engineering*, **4**, 192 (1985).
2. T. Narasimhaswamy and BSR Reddy, *Ind. J. Chem.*, **34B**, **607** (1995).
3. A. Mishra, TJM Sinha and V. J. Choudhary, *J. Appl. Polym. Sci.*, **527**, **68** (1998).
4. S. Agarwal, V. Choudhary and IK Verma, *Def. Sci. J.*, **47**, 401 (1997).
5. M. Patnaik, V. Choudary and IK Verma, *Euro Polym. J.*, **28**, 1433 (1992).
6. E. Strum, *Offen Ger.*, 2,523,093. See Also *Chem Abstr.*, **84**, 150522v (1976).
7. A. Pleurdean, C. Point and CM. Bruneau, *11th Int Conf Org Coat Sci Technol* 293-301, (1985), See Also *Chem Abstr.*, **105**, 210460n (1985).
8. P. Patel, B. Shah, A. Ray and R. M. Patel, *J. Polym. Research*, **11**, 65 (2004).
9. M. B. Patel, D. A. Patel and R. M. Patel, *Polym Int.*, **52(3)**, 367 (2003).
10. I. Erol, *J. Polym. Sci. Part A: Polym. Chem.*, **42(13)**, 3157 (2004).
11. C. Soykan and I. Erol, *J. Polym. Research*, **11(1)**, 53 (2004).
12. A. Bozkurt and B. Karadedeli, *Reactive and Functional Group*, **67(4)**, 348 (2007).
13. P. S. Vijayanand, S. Kato, S. Satokawa and T. Kojima, *Euro. Polym. J.*, **43(5)**, (2007).
14. U. Sentilkumar, K. Ganeshan and BSR Reddy, *J. Polym. Res.*, **10**, 21 (2003).
15. U. Sentilkumar, R. Balaji, A. Prasth and S. Nanyudan, *J. Macromol. Sci. Pure Appl. Chem.*, **38(1)**, 67 (2001) *Chem. Abstr.*, **134(25)**, 353624d (2001).
16. G. H. Stempel, R. P. Cross and R. P. Mareioll, *J. Am. Chem. Soc.*, **72**, 2299 (1950).
17. L. J. Bellamy, *Advances in Infrared Group Frequencies*, England: Methuen & Co Ltd., (1968).
18. G. H. Silverstein and F. X. Webster. *Spectrometric Identification of Organic Compounds*, 6th edition, New York: John Wiley & Sons Inc., (1998).
19. N. B. Colthup, L. H. Daly and S. E. Wiberley., *Introduction to Infrared Spectroscopy*, New York: Academic Press, (1990).
20. L. J. Bellamy. *The Infrared Spectra of Complex Molecules*, London: Chapman & Hall, (1975).
21. R. M. Silverstein, Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th edition; John Wiley & Sons, Inc.: New York, (1998).
22. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5(2)**, 259 (1950).
23. T. Kelen and F. Tudos, *J. Macro. Sci. Chem.*, **A9**, 1 (1975).
24. A. Briodo, *J. Polym. Sci.*, **A-2**, **7**, 1761 (1969).
25. C. D. Doyle., *Anal. Chem.*, **33**, 77 (1961).
26. L. Reich, *Die Makromol. Chem.*, **123**, 421 (1969).
27. J. Eric Lien, Corwin Hansch, S. M. Anderson, *J Medical Chem.*, **11(3)**, 430 (1968).