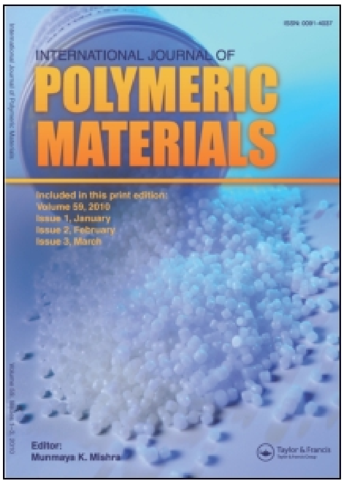

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Development and Applications of Novel Acrylic Copolymers

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To cite this Article Patel, Mitesh G. , Patel, Hetal J. , Patel, Jaimin R. , Patel, Kirit H. and Patel, Rajni M.(2008) 'Development and Applications of Novel Acrylic Copolymers', International Journal of Polymeric Materials, 57: 2, 165 — 176

To link to this Article: DOI: 10.1080/00914030701486179

URL: http://dx.doi.org/10.1080/00914030701486179

International Journal of Polymeric Materials, 57:165–176, 2008

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030701486179

Development and Applications of Novel Acrylic Copolymers

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The monomer 2,4-dichlorophenylacrylate was synthesized from 2,4-dichlorophenol and characterized by conventional methods. Homo- and copolymers of 2,4-dichlorophenylacrylate and butylmethacrylate were synthesized with different feed ratios using N,N-dimethylformamide as a solvent and 2,2′-azobisisobutyronitrile (AIBN) as an initiator at 70°C. The resulting polymers were characterized by infrared spectroscopy. Copolymer compositions were determined by ultraviolet (UV) spectroscopy. The monomer reactivity ratios were determined by applying the conventional linearization method of Fineman-Ross and Kelen-Tudos. The reactivity ratios values of 2,4-dichlorophenylacrylate and butylmethacrylate obtained from F-R plot are 0.91 and 1.15 respectively and from K-T plot, 0.97 and 1.24 respectively. The molecular weight and polydispersity of copolymers were determined by gel permeation chromatography (GPC). Thermo gravimetric analyses of the polymers were carried out in a nitrogen atmosphere. Thermal data suggest that the polymers underwent double decomposition. Homo and copolymers were tested for their antimicrobial properties against various microorganisms and showed strong inhibitory effects.

Keywords: copolymer, microbial screening, reactivity ratio, thermal analysis

INTRODUCTION

Acrylic and methacrylic esters are readily polymerized or copolymerized with a wide range of other monomers. The incorporation of

Received 20 May 2007; in final form 28 May 2007.

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two different monomers, having diverse physical and/or chemical properties in the same polymer molecule in varying proportions, leads to the formation of new materials with greater scientific and commercial importance [1,2]. The copolymers of acrylic and methacrylic esters have been used in various applications [3,4].

The chlorine-containing phenols and their derivatives possess antimicrobial properties and are used as fungicides, insecticides and algicides. 2,4-dichlorophenol, a well known biocide [5], has been anchored to a polymer by copolymerizing 2,4-dichlorophenylacrylate(2,4-DPA) with other vinyl monomers. Chlorine-containing phenylmethacrylate and its polymer have received considerable attention in recent years due to their varied applications [6,7]. These chemicals find applications as biocides. A copolymer of chlorophenylmethacrylate was used as base coat for leather [8]. Copolymers based on halogenated phenylacrylate have been utilized for synthesizing electroactive polymers for the preparation of polymeric reagents carrying piperazine and isonitrile functionalities [9,10]. Suzuki and Kato [11] prepared a number of copolymers containing 2,6-dichlorophenol which show good coating ability and provide high-quality color filter for liquid crystal display devices and solid-state image pick up devices. Patel et al. [12] prepared copolymers from 2,4-dichlorophenylmethacrylate with various vinyl monomers and reported that these polymers are useful as micro-biocides and are thermally stable up to 250°C.

The present work describes the synthesis and characterization of 2,4-dichlorophenylacrylate and butylmethacrylate monomers, their homopolymer and copolymers. The copolymer composition was determined by UV spectroscopy. The effects of 2,4-diphenylacrylate content in the copolymers on molecular weight and molecular weight distribution were examined by gel permeation chromatography. The thermal properties of the resulting copolymers have been investigated. Homo- and copolymers were also tested for their antimicrobial properties against selected microorganisms.

EXPERIMENTAL

Materials

Acrylic acid, benzoyl chloride (Chiti Chem.), 2,2′-azobisisobutyronitrile (AIBN, Aldrich), 2,4-dichlorophenol, hydroquinone(S.D.Fine Chemicals), and butylmethacrylate used were analytical grade reagents.

Synthesis of 2,4-dichlorophenylacrylate (2,4-DPA)

Acryloyl chloride was prepared according to the process reported in the literature [13]. The esterification of 2,4-dichlorophenol with acryloyl chloride was performed as follows:

Absolute alcohol (200 ml) and NaOH (0.1 mol, 4 gm) were placed in a three-necked flask equipped with a stirrer, condenser and thermometer. The content was stirred until all the NaOH was dissolved. To this mixture, 2,4-dichlorophenol (0.1 mol, 16.3 gm) was added. The reaction mixture was heated to 60°C for 30 min under stirring. Then it was cooled to room temperature and finally to 0–5°C. Freshly prepared acryloyl chloride (0.11 mol) was added drop-wise to the cooled reaction mixture and stirred for 90 min. It was then poured into a 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 anhydrous calcium chloride in a vacuum desiccator.

The formation of monomer was confirmed by IR spectroscopy and H^1-NMR techniques. IR (cm^{-1}): 3015(−CH stretching vibration of aromatic ring), 2978($v_{c=o}$) [14], 1640($v_{C=C}$), 1230(Asymmetric (v_{c-o-c}), 1150(symmetric v_{c-o-c}), 890(−CH bending mode of vinyl group), 730(rocking mode of vinyl group), 667(v_{c-cl}) [15]. The two absorption bands at 1593 and 1480 cm^{-1} may be assigned as the characteristic absorption of o-substituted phenyl ring [16,17].

H^1-NMR (ppm): 5.977(1H, −CH=), 6.357(1H) and 6.533(1H) (nonequivalent methylene protons), 7.158–7.432(3H, aromatic protons).

Copolymerization

Homo- and copolymerization were carried out in a solution using a free radical polymerization technique. Appropriate quantities of 2,4-dichlorophenylacrylate, butylmethacrylate N,N-dimethylformamide and 2,2′-azobisisobutyronitrile were mixed in a round-bottom flask equipped with a stirrer and reflux condenser. The reaction mixture was heated at 70°C for 5 hr under stirring. It was then poured into a large volume of methanol with stirring. When the polymer was precipitated out it was filtered and washed with methanol. Solid polymer was purified by repeated precipitation by methanol from solution in toluene and finally dried under vacuum. The synthesis of homo- and copolymer is represented in Figure 1.

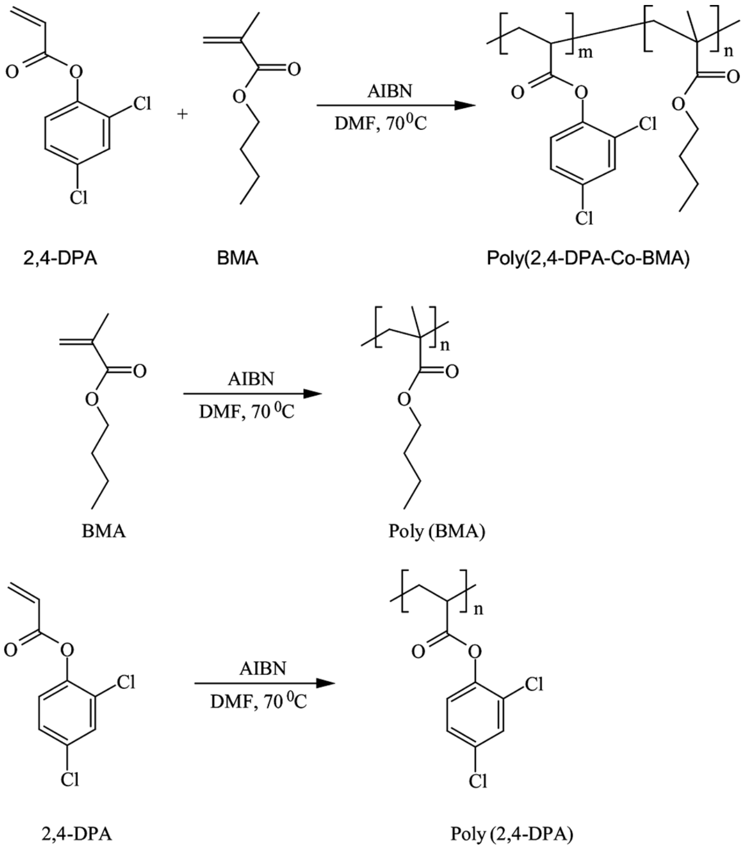

FIGURE 1 Reaction scheme.

Characterization

NICOLET 400_D FT-IR spectrophotometer was used to record the infrared spectrum of homo- and copolymers on solid KBr pellets. Copolymer composition and reactivity ratios were determined using Shimadzu-160-A UV-visible spectrophotometer. GPC instrument was employed for the determination of molecular weight of the polymers. Dimethylformamide (DMF) at 1.0 ml/min flow rate was used as a mobile phase throughout the analysis. All the measurements were carried out at 30°C temperature. TA instruments (USA)-2960 thermo gravimetric analyzer was used to record the thermograms of polymers at a heating rate of 10°C/min in a nitrogen atmosphere. DTA was performed with a TA instrument (USA)-2960 differential analyzer at a heating rate of 10°C/min under a nitrogen atmosphere.

Microbial Screening

Polymers synthesized by different experimental conditions were tested for their effect on the growth of various microorganisms. Their interactive roles with bacteria (*Bacillus subtilis, Escherichia coli* and *Staphylococcus citreus*), fungi (*Aspergillus niger, Sporotichum pulveruletum* and *Trichocerma lignorum*) and yeast (*Candida utilis, Saccharomyces cerevisiac* and *Pichia stipitis*) were also investigated.

Screening of Acrylic Copolymer for Antibacterial Activity

5% (v/v) inoculum of bacterial culture was used to inoculate 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 aliquotes were withdrawn at a specified time intervals (20–48 hr) from test media. After suitable dilution with distilled water, optical density was measured at 660 nm and calculated as optical density per ml (i.e. growth). The method is based on the principle that as the growth proceeds, cell number increases which leads to an increase in optical density of medium. The percentage inhibition for bacteria was calculated by the following formula:

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

where X = optical density of bacterial suspension in control set, and Y = optical density of bacterial suspension in test set.

Screening of Acrylic Copolymer for Antifungal Activity

Since fungal culture shows filamentous growth, the optical method can not be 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 hr. The contents of the 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, and Y = weight of dry fungal cell mass in test set.

Screening of Acrylic Copolymers on Yeast

A 5% (v/v) inoculum of yeast culture was added to the sterile control medium and test medium (100 ml control + 50 mg polymer) and the same procedure as given in the reaction on antibacterial activity was followed.

RESULTS AND DISCUSSION

The IR spectra confirm the structure of copolymers in all aspects: A band at 3080 cm^{-1}, which could be due to C–H stretching in the aromatic ring; The bands at 1582 and 1491 cm^{-1} could be assigned as the C–C stretching in the phenyl ring; the bands at 863–876 and 822–841 cm^{-1} are due to C–H out of plane bending in the phenyl ring; Broad bands at 2958–2993 and 2925–2947 cm^{-1} could be due to C–H stretching in the alkyl group; a band at 1466 cm^{-1} is due to the asymmetric stretching of the methyl and methylene group; a band at 1380 cm^{-1} is due to symmetric stretching of the methyl group. Two strong absorptions, one at 1723 and other at 1770 cm^{-1}, are due to the –C=O stretching of the ester group; a band between 1215–1241 cm^{-1} is due to C–O–C starching; and a band at 670 cm^{-1} is due to the C–CI stretching [18].

Copolymer Composition and Reactivity Ratios

The average composition of each copolymer sample was determined from the corresponding UV spectroscopy. The assignment of the absorption in the UV spectrum allows the accurate evaluation of the content of each kind of monomeric unit incorporated into the polymer chains. From monomer feed ratios and copolymer compositions, the reactivity ratios of 2,4-DPA and butylmethacrylate were determined by the Fineman and Ross [19] and Kelen and Tudos [20] method and are presented in Table 1. The values of reactivity ratios for 2,4-DPA (r_1) and BMA(r_2) are 0.91 and 1.15 respectively from F-R plot

TABLE 1 Copolymer Composition Data and Reactivity Ratios of Copolymers of 2,4-DPA and BMA

Sample code no.	Monomer feed composition: 2,4-DPA $[M_1]$ mole	Monomer feed composition: BMA $[M_2]$ mole	Conversion %	Composition of 2,4-DPA in copolymer $[m_1]$	Reactivity ratios F-R r_1	Reactivity ratios F-R r_2	Reactivity ratios K-T r_1	Reactivity ratios K-T r_2
1	1.0	–	–	–	0.91	1.15	0.97	1.24
2	0.2	0.8	8.28	0.165				
3	0.4	0.6	8.59	0.378				
4	0.5	0.5	9.23	0.472				
5	0.6	0.4	9.56	0.586				
6	0.8	0.2	8.68	0.781				
7	–	1.0	–	–				

and 0.97 and 1.24 respectively from K-T plot. As the value of r_1 is less than r_2, in this system BMA is found to have higher reactivity than 2,4-DPA. The values of r_2 are greater than 1 and the product of r_1r_2 is also greater than 1. This indicates that the copolymers are weak orders with predominantly random distribution of monomeric units in the polymeric chain.

Molecular Weights and Viscosity Measurements

The number and weight average molecular weight of homo- and copolymers of 2,4-dichlorophenylacrylate with butylmethacrylate were obtained from gel permeation chromatography. The values of number average and weight average molecular weight range from 31880 to 38520 gm/mol and 45190 to 57910 gm/mol respectively whereas the polydispersity index ranges from 1.334 to 1.503. Molecular weight data are presented in Table 2. It is observed from these results that

TABLE 2 Average Molecular Weights by GPC for the Copolymers of 2,4-DPA with BMA

Sample code no.	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mz}$	Polydispersity index	Intrinsic viscosity $[\eta]$ dl.g^{-1}
1	32380	48640	63870	1.502	0.2100
2	31880	45190	56840	1.418	0.1924
4	33980	47480	61590	1.398	0.2035
6	36940	49290	62110	1.334	0.2200
7	38520	57910	77680	1.503	0.2422

the molecular weight increases as 2,4-DPA content increases in the copolymer, whereas the polydispersity index changed randomly.

Thermal Analysis

Thermal behavior of the homo- and copolymer was studied by TGA (Thermogravimetric analysis) and DTA (Differential thermal analysis). Selected samples were taken for the thermal analysis.

Thermogravimetric Analysis (TGA)

The data in Table 3 indicate that the polymers underwent two-step decomposition. Activation energy and integral procedural decomposition temperature (IPDT) were determined by Broido's [21] and Doyle's [22] method, respectively. Thermal studies showed that the polymers underwent decomposition in the range 191–424°C. The activation energy for the polymers is in the range 71–76 $KJmol^{-1}$. The IPDT value for the polymers is in the range 367–379°C.

Differential Thermal Analysis (DTA)

Differential thermal analysis results from homo- and copolymers were determined by Reich's [23] method. The activation energy of polymers

TABLE 3 TGA Data for Homo- and Copolymers of 2,4-DPA and BMA

Sample code no.	% Weight loss at various temperature (°C) 200	300	400	500	600	Decomposition temperature range (°C)	T_{max}[a] (°C)	T_{50}[b] (°C)	IPDT[c] (°C)	Activation energy[d] (E_A) (KJ $mole^{-1}$)
1	1	6	79	87	92	191–340 341–424	389	383	403	75
2	2	13	88	98	99	276–422	358	356	367	71
4	5	20	90	96	99	185–282 283–415	356	353	370	73
6	7	22	88	94	99	204–285 286–408	357	350	379	76
7	1	44	94	99	99	212–438	315	312	346	80

[a] Temperature for maximum rate of decomposition.
[b] Temperature for 50% weight loss.
[c] Integral procedural decomposition temperature.
[d] By Broido's method.

TABLE 4 DTA Data for Homo- and Copolymers of 2,4-DPA and BMA

Sample code no.	$T_1{}^a$ (°C)	$T_2{}^b$ (°C)	$T_b{}^c$ (°C)	Activation energy[d] (E_A) (KJ mol^{-1})	Reaction order
1	385	440	412	76	1
2	366	433	425	76	1
	438	445	480	37	1
4	360	432	401	80	1
	472	565	514	44	1
6	354	410	382	83	1
	482	568	515	34	1
7	298	380	358	85	1
	384	497	432	40	1

[a] Starting temperature of DTA.
[b] Ending temperature of DTA.
[c] Peak maximum temperature of DTA trace.
[d] Activation energy by Reich's method.

of thermal degradation ranged from 34–85 KJmol^{-1} and the reaction is a first order reaction.

Thermal data in Table 4 suggested that homo- and copolymers follow a two-step degradation and possess a moderate stability. It is also observed that incorporation of 2,4-DPA in polymers does not change their thermal stability with respect to their individual homopolymers to any significant extent.

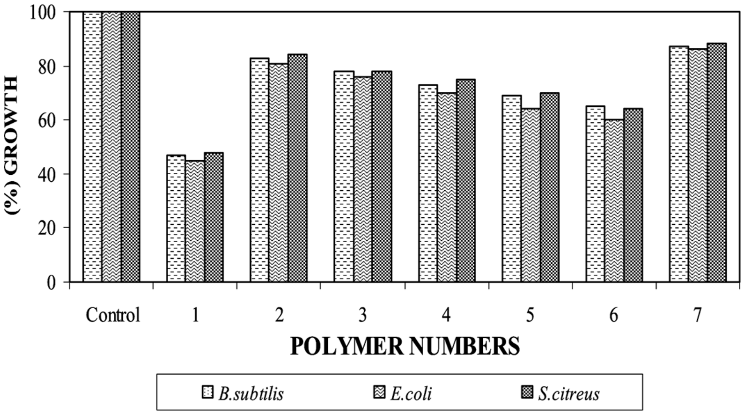

FIGURE 2 Effect of 2,4-DPA-co-BMA homo- and copolymers on growth (%) of bacteria.

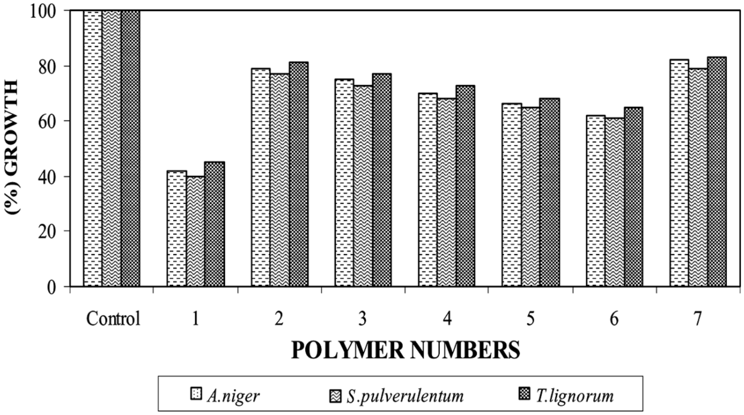

FIGURE 3 Effect of 2,4-DPA-co-BMA homo- and copolymers on growth (%) of fungi.

Microbial Screening

A microbial screening on the homo- and copolymer of 2,4-DPA and BMA was carried out. The obtained results are presented in Figure 2, 3 and 4 respectively for bacteria, fungi and yeast. Poly (2,4-DPA) allows 47% growth for bacteria and poly(BMA) allows 86% growth for bacteria, whereas its copolymer favors 63–81% growth. Fungi shows 43% growth for poly (2,4-DPA), 82% growth for poly(BMA) and 63–79% growth for copolymers. Yeast shows 40%

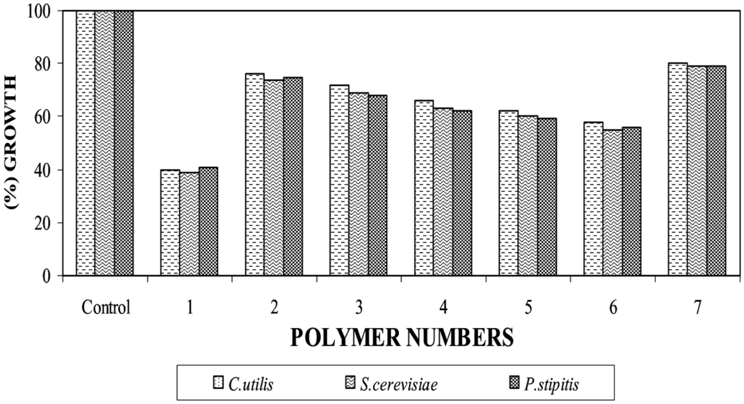

FIGURE 4 Effect of 2,4-DPA-co-BMA homo- and copolymers on growth (%) of yeast.

growth for poly (2,4-DPA), 79% growth for poly(BMA) and 56–74% growth for copolymers.

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

CONCLUSION

The monomer 2,4-DPA was synthesized, characterized and copolymerized with BMA by free radical polymerization using different feed ratios. Conventional methods were employed to characterize the polymers. The reactivity ratio of 2,4-DPA is less than that of BMA, and the product of reactivity ratios was greater than one. This indicates the copolymers are weak orders with a predominantly random distribution of monomeric units in the chain. The GPC results show that as 2,4-DPA content in copolymer increases, the molecular weight also increases. TGA data reveal that the copolymer undergoes two-step degradation. Chlorine content is important to impart antimicrobial property in these polymers. Among the polymers investigated, the homopolymer of 2,4-DPA is the most effective antimicrobial agent.

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