

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis and Rheological Studies of Methacrylic Acid-Ethyl Acrylate-Allyl Methacrylate Terpolymers

Y. K. Agarwal<sup>a</sup>; S. D. Kaushik<sup>b</sup>; P. C. Kumar<sup>a</sup>

<sup>a</sup> Department of Chemistry, Raj Kumar Goel Institute of Technology, U. P. Technical University, Ghaziabad, India <sup>b</sup> Department of Chemistry, L. R (P.G) College, C. C. S. University, Sahibabad, India

**To cite this Article** Agarwal, Y. K. , Kaushik, S. D. and Kumar, P. C.(2007) 'Synthesis and Rheological Studies of Methacrylic Acid-Ethyl Acrylate-Allyl Methacrylate Terpolymers', Journal of Macromolecular Science, Part A, 44: 8, 877 – 880

**To link to this Article:** DOI: 10.1080/10601320701407896

**URL:** <http://dx.doi.org/10.1080/10601320701407896>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Synthesis and Rheological Studies of Methacrylic Acid-Ethyl Acrylate–Allyl Methacrylate Terpolymers

Y. K. AGARWAL,<sup>1</sup> S. D. KAUSHIK,<sup>2</sup> and P. C. KUMAR<sup>1</sup>

<sup>1</sup>Department of Chemistry, Raj Kumar Goel Institute of Technology, U. P. Technical University, Ghaziabad, India

<sup>2</sup>Department of Chemistry, L. R (P.G) College, C. C. S. University, Sahibabad, India

Received November, 2006, Accepted January, 2007

Methacrylic acid-ethyl acrylate-allyl methacrylate terpolymers were synthesized by using precipitation polymerization using toluene as the solvent. The rheological studies of the synthesized polymers were made using Brookfield viscometer at 20 rpm and room temperature ( $30 \pm 1^\circ\text{C}$ ). Crosslinked polymers (1% w/w) were mixed with water and the pH of the solution was raised to 7.5–8.2 by the addition of 28% solution of ammonia. The effect of various factors like methacrylic acid content, crosslinking agent (AMA) content, solid content, shear rate, pH and electrolyte concentration added on viscosity was studied.

**Keywords:** methacrylic acid; ethyl acrylate; allyl methacrylate; rheological studies

## 1 Introduction

Copolymerization of hydrophobic monomers e.g., ethyl acrylate (EA), butyl acrylate (BA), styrene, acrylonitrile (AN), a small amount of hydrophilic vinyl acid monomers e.g., acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) has been reported in the literature (1–5). MAA/AA polymers and copolymers are of commercial interest due to their application in adhesives, binders, dispersants, thickeners, flocculants, etc. (6).

Polysaccharides of natural origin, namely alginate, guar gum, cellulose, modified starch and locust bean gum are well known thickening agents in textile printing. All these natural thickeners are being used for printing with reactive as well as disperse dyes. But these could not be used for pigment printing, because they result in print dullness and poor fastness properties. Emulsion thickening containing 80% (w/w) of kerosene is the suitable thickener for pigment printing, although it causes air pollution, since all the kerosene is driven into the atmosphere during drying and curing processes.

Copolymers of MAA/AA have received significant attention, particularly in the field of pigment printing as synthetic thickeners. The most prevalent commercial process to make such polymers is the solution polymerization of MAA/AA in the presence of a solvent for monomers (7). Various solvents

like toluene (8), benzene (9) etc. have been used for the polymerization of acrylic acid/alkyl acrylates. MAA/AA appears to be the major constituent of these thickeners, since it is responsible for the development of viscosity on neutralization with a base (e.g., liquor ammonia) (10). The free carboxylic acid groups on neutralization convert into carboxylate anions, which repel each other. Due to repelling of these anions, polymer chains get uncoiled and high viscosity developed.

Synthetic thickeners used in pigment printing are pseudoplastic in nature i.e., show shear thinning behavior, which is estimated as thixotropy. The thixotropy of methacrylic acid-methyl acrylate copolymer was reported (11) to be 7.6 estimated by the ratio of viscosity at 50 rpm to that of 1000 rpm. Rheological properties of acrylic based polymers have been reported in many research papers (12–18). Literature studies (19–21) show that most of the synthetic thickeners are crosslinked polymers, since crosslinked polymers showed the printable viscosity at a low solid content.

This paper describes the synthesis and rheological behavior of methacrylic acid–ethyl acrylate polymers crosslinked with allyl methacrylate (AMA) using the precipitation polymerization technique. Polymers of varying MAA/EA ratios and degree of crosslink density (AMA) were synthesized.

## 2 Experimental

### 2.1 Materials

Methacrylic acid (CDH, India) and ethyl acrylate (CDH, India) were used as monomers. Allyl methacrylate (MERCK-

Address correspondence to: Y. K. Agarwal, Department of Chemistry, Raj Kumar Goel Institute of Technology, U. P. Technical University, Ghaziabad (U.P.), 201003, India. Fax: +91-0120-2788447; E-mail: yogeshkag@yahoo.com

**Table 1.** Polymerization recipe

Compound	Weight (g)
Methacrylic acid	100–140
Ethyl acrylate	60–110
Allyl methacrylate	1.5–3.5
2,2' Azobisisobutyronitrile (AIBN)	0.30
Toluene	800

Schuchardt) was used as a crosslinking agent and 2,2'-Azobisisobutyronitrile (AIBN) (High Polymer Labs, India) was used as initiator. Toluene (Qualigens Fine Chemicals, India) was used as a solvent. All chemicals were used as received.

## 2.2 Synthesis of Crosslinked Polymers

Methacrylic acid-ethyl acrylate-allyl methacrylate terpolymers with varying amounts of MAA/EA/AMA were synthesized by using a precipitation polymerization technique as per the polymerization recipe for 1000 g batch (Table 1). Initially, 800 g of toluene was taken in a three-necked glass reactor fitted with a mechanical stirrer, thermometer, reflux condenser, and a dropping funnel, and placed in a heating mantle. Monomers MAA, EA, and AMA were mixed. 150 g of this mixer was added to the refluxing toluene at 110–111°C. In the rest of monomers mixer, 0.30 g of AIBN was mixed. This solution was added to the glass reactor drop by drop in 3 h. The stirrer speed was kept at 120 rpm. The temperature of the glass reactor was maintained at 110–111°C. A holding time of 2 h was provided. The polymer formed was separated through filtration with the help of Buckner funnel using Wattman 40 filter paper as fine solid powder. The yield was above 90% in all the experiments. Monomer feed ratios as practically appointed and codes for all the polymers are given in Table 2.

## 2.3 Measurement of Viscosity

Crosslinked polymers (1% w/w) were mixed with water and the pH of the solution was raised to 7.5–8.2 by the addition of 28% solution of ammonia. Viscosity of these solutions was measured by using a Brookfield RVT viscometer at 20 rpm and room temperature ( $30 \pm 1^\circ\text{C}$ ).

The viscosity at different pH values was measured. Viscosity was also measured at different rpm (2.5–50) to study the shear thinning behavior. Viscosity was also measured in the presence of 0.5–1.5% NaCl to study the effect of electrolytes added on viscosity.

## 3 Results and Discussion

### 3.1 Brookfield Viscosity of Polymers

The Brookfield viscosity of all the polymers (P1 to P8) was measured at 20 rpm. The viscosity was found to increase

**Table 2.** Polymer codes, monomer feed ratios and brookfield viscosity of polymers

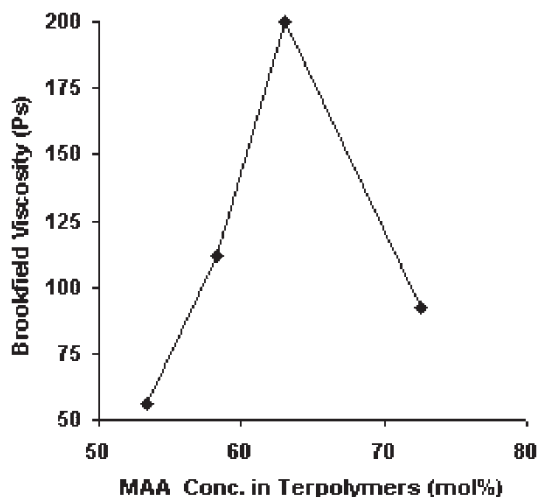
Polymer code	Monomer feed ratio (Mol%)			Brookfield viscosity (Ps)
	MAA	EA	AMA	
P1	53.37	45.90	0.73	56
P2	58.27	41.00	0.73	112
P3	63.10	36.17	0.73	200
P4	72.53	26.74	0.73	92
P5	63.21	36.24	0.55	40
P6	62.98	36.11	0.91	250
P7	62.87	36.04	1.09	340
P8	62.75	35.98	1.27	550

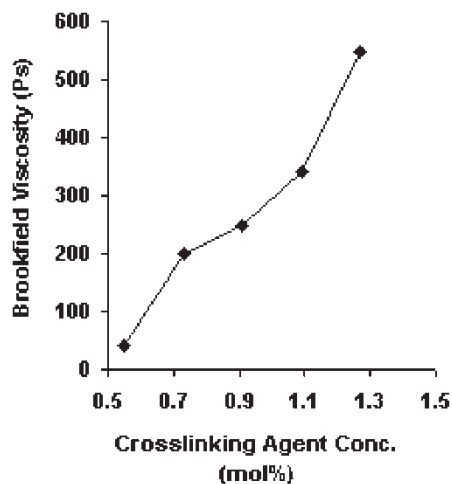
from a 56 to 200 Ps with an increase in the MAA content from 53.37 (P1) to 63.10 (P3) mol% and thereafter, it decreases to a 92 Ps for the polymer containing 72.53 (P4) mol% MAA content (Figure 1). AMA content (crosslinker) in all of these polymers (P1 to P4) was kept 0.73 mol%. These results clearly show that 63.10 mol% is the optimum concentration of MAA.

In the acidic state, long chain of polymer remains in coiled form. On neutralization with ammonia solution, the chain becomes polyanionic and under the action of strong repulsive force, straightening and separation of chain occurs to a maximum possible extent. At a high concentration of MAA, ammonium carboxylate groups formed lead to dissolution of polymer into water in place of the chain extension, therefore, resulting in lower viscosity.

### 3.2 Effect of Crosslinking Agent Concentration on Brookfield Viscosity

The crosslinking agent (AMA) concentration was varied from 0.55 to 1.27 mol% (P5, P3, P6–P8) for the optimum composition of MAA-EA. The Brookfield viscosity of all these

**Fig. 1.** Effect of MAA content on the Brookfield viscosity.

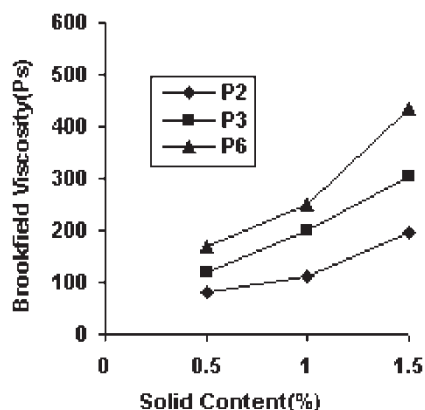


**Fig. 2.** Effect of crosslinking agent (AMA) concentration on Brookfield viscosity.

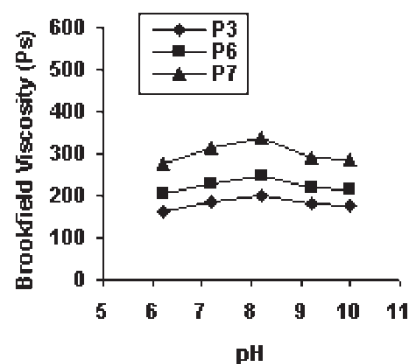
polymers was found to increase from 40 to 550 Ps with an increase in the concentration of AMA from 0.55 to 1.27 mol% (Figure 2). The small degree of crosslinking agent binds the polymer chains together. Due to crosslinking, they act as hydrated particles with more than hundred fold expansion of their original size. The high viscosity results because loosely crosslinked long chain acrylic polymer molecules undergo swollen in the entangled form.

### 3.3 Effect of Solid Content on Brookfield Viscosity

To study the effect of solid content on Brookfield viscosity, the amount of the three polymers (P2, P3, and P6) was varied from 0.5 to 1.5%. Brookfield viscosity was found to increase with an increase in the solid content of the polymer in all the cases (Figure 3). The viscosity curve shows a steep rise in viscosity with the increase in solid content from 0.5 to 1.5%. The polymer chains in the solution are completely enveloped by the solvent and there is a critical concentration at which no free solvent is left.



**Fig. 3.** Effect of solid content on the Brookfield viscosity of polymers (P2, P3, P6).



**Fig. 4.** Effect of pH on Brookfield viscosity of polymers (P3, P6, P7) at 20 rpm.

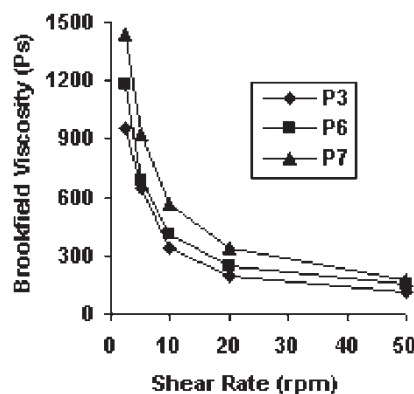
Above this concentration, polymer chains are tightly packed together which results in the development of very high viscosity.

### 3.4 Effect of pH on Brookfield Viscosity

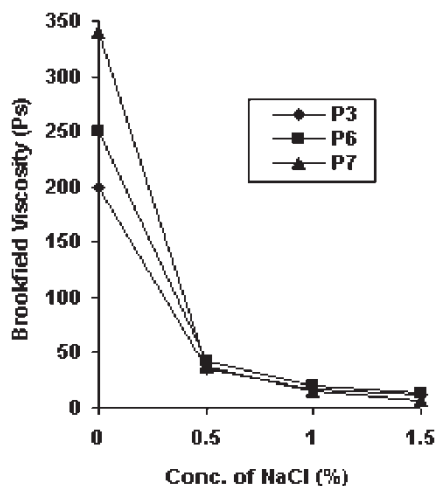
Brookfield viscosity of the three polymers (P3, P6, and P7) was measured over a wide range of pH values (6–10.5) at 20 rpm. Viscosity was found to increase with an increase in the pH value of the solution up to 8.2 and beyond that viscosity was found to decrease with any increase in the pH value (Figure 4). Therefore, the optimum range of the pH value is 7.5–8.2. Polymer chains reached its maximum swelling at pH 7.5–8.2, after this value polymer chains disintegrate into a true solution upon addition of more base.

### 3.5 Effect of Shear Rate on Brookfield Viscosity

To study the effect of the shear rate, the Brookfield viscosity of the three polymers (P3, P6, and P7) was measured at different rpm (2.5–50). Viscosity of all these polymers was found to decrease with the increase in shear rate. Figure 5 clearly shows that the nature of these polymers is pseudoplastic. This behavior can be explained by Ostwald-de Waele-Nutting models (power-law), a two-parameter model for



**Fig. 5.** Effect of shear rate on Brookfield viscosity of polymers (P3, P6, P7).



**Fig. 6.** Effect of electrolyte concentration on the Brookfield viscosity of polymers (P3, P6, P7).

describing pseudoplastic behavior (22–23).

$$\eta = k \cdot \gamma^{n-1}$$

Where  $\eta$  is viscosity,  $k$  is consistency or viscosity coefficient,  $\gamma$  is shear rate and  $n$  is flow behavior index.

For a shear-thinning fluid, the index may have any value between 0 and 1. Smaller the value of  $n$ , the greater is the degree of shear thinning. Power law relation describes flow curves (Figure 5). Viscosity decreases with the increase of shear rate and viscosity ( $\eta$ ) is maximum when shear rate ( $\gamma$ )  $\rightarrow$  0.

### 3.6 Effect of Electrolyte on Brookfield Viscosity

Brookfield viscosity of the three polymers (P3, P6, and P7) was measured in the presence of 0.5–1.5% of sodium chloride (NaCl) at 20 rpm. Viscosity was found to decrease drastically on addition of NaCl (Figure 6). Because of regression of the carboxyl group's dissociation, repulsive force decreases and polymer chains start recoiling which results in the drastic drop in viscosity.

## 4 Conclusions

Methacrylic acid-ethyl acrylate-allyl methacrylate terpolymers with varying amounts of MAA/EA/AMA were synthesized by using precipitation polymerization. The effect of various factors such as carboxylic acid content, crosslinking agent concentration, solid content, shear rate, pH and electrolyte concentration on the Brookfield viscosity was studied. The viscosity of these polymers was found to depend on the methacrylic acid content. The viscosity increased with the increase in crosslinking agent (AMA) concentration. The viscosity increased with the increase in the solid content of the solution. The viscosity decreased with the

increase in shear rate, therefore these polymers showed pseudoplastic behavior. The viscosity was found to be maximum in the pH range of 7.5 – 8.2. A drastic decrease in the viscosity was found on addition of the electrolyte.

## 5 References

- Sivankova, R.P., Lyubliner, M.A., Khomich, L.F., and Drobova, L.A. USSR Patent, (1982) 979,551; Chem. Abstr., 1983, **98**, 162, 373z.
- Bajaj, P. and Kumari, S. (1987) *J.M.S.-Rev. Macromol. Chem. Phys.*, **C 27(2)**, 181.
- Chang, C.J. and Stevens, E.T. (Rohm and Haas Co.); U.S. Patent, 1983, 4, 423, 199; Chem. Abstr., 1984, **100**, 121780w.
- Ruffner, C.G. (Alco Standard Corp.) U.S. Patent, 1986 4, 616,074; Chem. Abstr., 1987, **106**, 85255s.
- Drahomir, D., Cerovsky, K., and Civin, P. Czechoslovakian Patent, 1989, 258, 537; Chem. Abstr., 1990, **112**, 79372k.
- Liu, T., Desimone, J.M. and Roberts, G.W. (2006) *Polymer*, **47(12)**, 4276–4281.
- Swift, G. In *Acrylic (and Methacrylic) Acid Polymers, Encyclopedia of Polymer Sciences and Technology*; Bailey, J. and Kroschwitz, J.I. (eds.); Hoboken, Wiley: New York, Vol. 1, 79–96, 2003.
- Dammann, L.G. (1982) (Clean Corp.) U.S. Patent. 4, 338, 239 Chem. Abstr., 1982, 97, 129, 076m.
- Huang, C. and Schaltzer, R.K. (B.F. Goodrich Co.) South African Patent, (1984), A8, 306, 734 Chem. Abstr., 102, 115, 099f.
- Chavan, R.B., Bajaj, P. and Goyal, M. (1994) *Indian Jour. of Fibre Text. Res.*, **19**, 22–29.
- Tao Gosei Chem. Ind. Co., Japanese Patent (1989) 82139110; Chem. Abstr., 1983, 98, 54691.
- Bajaj, P., Goyal, M. and Chavan, R.B. (1993) *J.M.S.-Rev. Macromol. Chem. Phys.*, **C 33(3)**, 321–348.
- Xingm, L., Chenm, M., Glassm, J.E., Buchacekm, R.J. and Dickinsonm, J.G. (1998) *Polym. Mater. Sci. Eng.*, **79**, 413; Chem. Abstr., 1998, 129, 232014t.
- Deshpande, S.D. and Mishra, R.C. (1993) *Man-Made Text. Ind.*, **36(12)**, 517.
- Clarke, J. (1994) *Surf. Coat. Int.*, **77(7)**, 303.
- Schneider, R. (1997) *Textilveredlung*, **32(3/4)**, 66; Chem. Abstr., 1997, 126, 331589d.
- Qyadrat, O., Mrkvickova, L. and Walterova, Z. (1998) *Colloid Polym. Sci.*, **276(10)**, 879.
- Makarewicz, E. (1999) *Przem. Chem.*, **78(3)**, 100; Chem. Abstr., 1999, 131, 89101c.
- Langerbeins, K., Hans, T., Josef, K., and Wolfgang, K.. Rochm GmbH European Patent, 1990, 398151; Chem. Abstr., 1991, 114, 83552c.
- Bajaj, P., Chavan, R.B. and Bhatia, M. (1986) *Text. Res. J.*, **56**, 63.
- Yokoyama, F., Achife, C.E., Takahira, K., Yamashita, Y. and Monobe, K. (1992) *J. Macromol. Sci.-Phys. B*, **31(4)**, 463–483.
- Hackley, V.A. and Ferraris, C.F. *Guide to Rheological Nomenclature: Measurements in Ceramic Particulate Systems*; NIST Special Publication 946; 2001.
- Fried, J.R. *Polymer Science and Technology*; PHI Pvt. Ltd.: New Delhi, 2002.