



Asian Journal of Chemistry; Vol. 28, No. 7 (2016), 1607-1610

ASIAN JOURNAL OF CHEMISTRY

<http://dx.doi.org/10.14233/ajchem.2016.19769>



Studies on Thermal, Microbial Behaviours of Copoly(azo-maleimide-Acrylic Acid/Vinyl Acetate) and Terpoly(azo-maleimide-acrylic acid-vinyl acetate): Synthesis and Characterization

JYOTI CHAUDHARY, SUMAN JINGER*, SWATI PUROHIT and HARSHADA JOSHI

Department of Polymer Science, Mohanlal Sukhadia University, Udaipur-313 001, India

*Corresponding author: E-mail: sumanjinger@gmail.com

Received: 19 December 2015;

Accepted: 8 February 2016;

Published online: 31 March 2016;

AJC-17858

A terpolymer based on polymerizable monomer unit of N-substituted maleimide associated with azo moiety as a pendent group, acrylic acid and vinyl acetate was chemically architected. The preparation of terpolymer was accelerated by free radical polymerization using AIBN initiator at 70 ± 2 °C in THF solvent. Copolymers of maleimide with acrylic acid/vinyl acetate have also been synthesized, characterized and results were comparatively analyzed with terpolymer. The thermal properties of terpolymer and copolymers such as glass transition temperature (T_g) and thermal decomposition were determined by DSC and TGA analysis respectively. The weight molecular weight (M_w) and number average molecular weight (M_n) were determined by gel permeation chromatography. Density measurement, solubility test, viscosity test, elemental analysis, FT-IR, ^1H NMR spectral analysis were used to characterization of terpolymer and copolymers.

Keywords: Terpolymer, Copolymer, Maleimide, Acrylic acid, Vinyl acetate, TGA, DSC.

INTRODUCTION

It has been a great interest to developed a variety of synthetic route to form olefinic-imide frames known as maleimide using different derivatives of amines and modified to achieved multi-functionalities in N-substituted maleimide polymers [1-3]. N-substituted maleimides and derivatives with acrylates have been extensively used in polymerization reactions to form thermally stable, high performing synthetic materials such as high strength composites, molding composites, adhesives and also production of superabsorbent polymers, oil treatment chemicals, water treatment chemicals, detergent intermediates and water absorbent polyacrylic acid polymer [4]. A few copolymers and terpolymers of N-substituted maleimide containing monomer, acrylic acid and vinyl acetate have been synthesized to investigate their applicability areas in high performance materials as a thermally stable and resist materials towards microbial conditions [5-7], which is influenced by hydrogen bond interaction [8,9].

In the present study, we are mainly concerned with the influence of H-bonding on the structure and glass transition temperature (T_g) of newly copolymers and terpolymer consisting of N-substituted maleimide with acrylates and vinyls. Acrylic acid (AA) and vinyl acetate (VA) into polymeric chain of maleimide were introduced to increase the thermal performance with high flexibility and also analyzed microbial

activities. In this paper, we report the synthesis of homopolymer 4-N-phenylethanamideazo-3-N-(4-nitrophenyl)maleimide [HPANMI], copolymers [4-N-phenylethanamideazo-3-N-(4-nitrophenyl)maleimide-co-acrylic acid] [C_1 PANMI], [4-N-phenylethanamideazo-3-N-(4-nitrophenyl)maleimide-co-vinylacetate] [C_2 PANMI], and terpolymer [4-N-phenylethanamideazo-3-N-(4-nitrophenyl)maleimide-acrylic acid-vinyl-acetate] [T_1 PANMI], using free radical initiator and organic polar solvent.

EXPERIMENTAL

p-Amino acetanilide and maleic anhydride were recrystallized from acetone (LobaChemei, AR). AIBN (Fisher Scientific, AR), THF, DMF and methanol (Sigma Aldrich, AR) are used without any purification.

Synthesis of N-(4-N-phenyl ethanamide)maleimide [PEMI] (I): The N-(4-N-phenyl ethanamide) maleimide PEMI (I) was prepared by the reaction of *p*-amino acetanilide (0.1 mol) and maleic anhydride (0.1 mol) according to reported method [10]. The monomer N(4-N-phenyl ethanamide azo-3-N-(4-nitro phenyl)maleimide [PANMI] (II) was synthesized by diazotization reaction (**Scheme-I**). Copolymerization and terpolymerization were carried out to form polymers of PANMI accompanied by THF solvent and AIBN initiator at 60-70 °C (**Schemes I and II**). Resulting polymers appearance are orange-brown colour.

Yield of polymerization: The percentage yield was differed in polymerization process of homopolymer, copolymers and terpolymer which are refer to the using different solvent-initiator couples-system and according the production, It was observed that the percentage yield in THF-AIBN system is high as compared to DMF, 1,4-dioxane solvents.

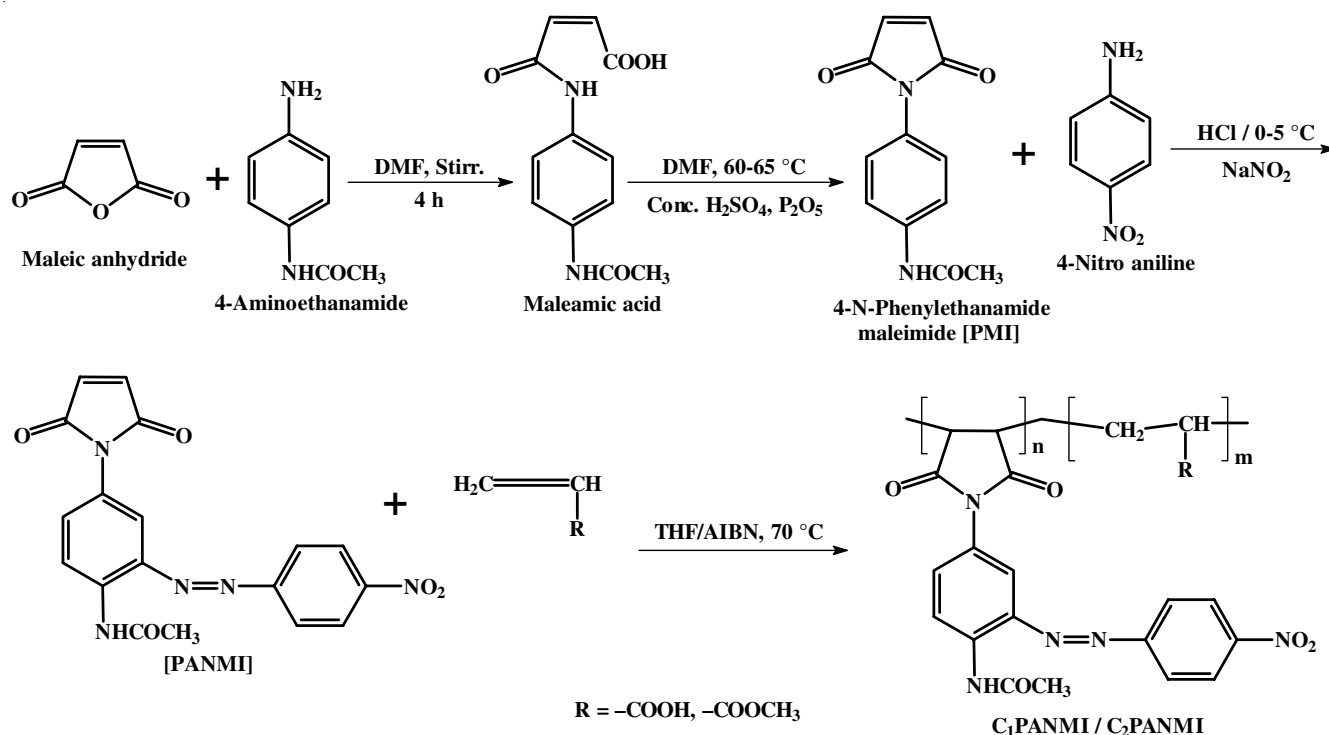
RESULTS AND DISCUSSION

Infrared spectra were recorded on a FTIR Perkin Elmer spectrometer mode RX-I using KBr pellets for sample preparation. The spectrum information was collected in the range of 4000–250 cm^{-1} . The ^1H NMR spectral data was recorded in $\text{DMSO}-d_6$ with TMS as an internal standard reference. Spectra and spectral values are shown in Table-1. The peak of double bonded carbons in five membered imide ring was disappear in homopolymer, copolymers and terpolymer pervasive the polymerized and unpolymerized units and enable to polymerization in concern compounds at double bonded carbon atoms. The hydrogen bonding shown between carbonyl-oxygen and hydroxyl-hydrogen, confirmed by the carbonyl stretching bands are shifted in downward zone with broad absorption

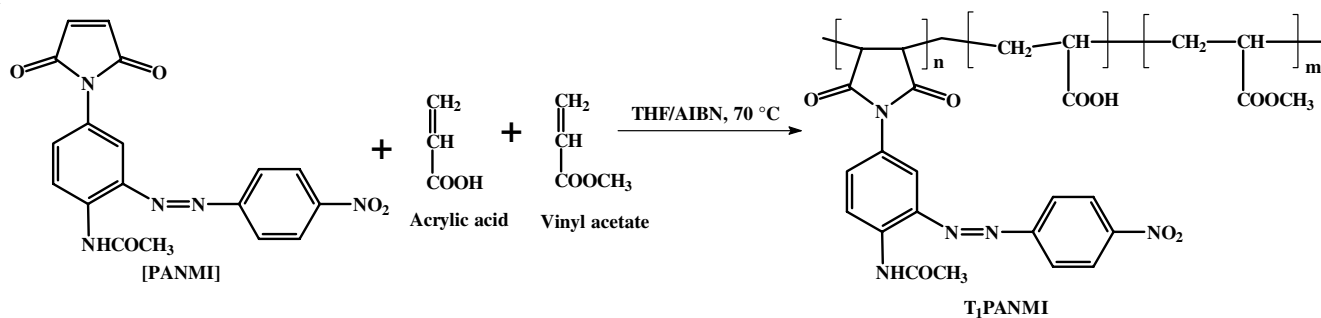
band. Stronger the hydrogen bond, greater the absorption and peak was shifted towards lower wave number than the normal absorption peak.

Physical properties: Solubility of homopolymer, copolymers and terpolymer was examined in our laboratory by using solvents of varying parameters and it seems that these were perfectly soluble in THF, DMF, DMSO and partially soluble in acetone, 1,4-dioxane and ethyl acetate. Some other characterization like viscosity, density also determined. Molecular weight was measured by gel permeation chromatography (GPC) technique. The molecular weight distribution in polymers varies from very low to very high range of molecular weight. Poly dispersity index of all polymers were also determined by same technique. Terpolymer reveals high molecular weight due to presence of three co-monomer units to create dense molecular structure. The number average molecular weight (M_n), weight average molecular weight (M_w) and poly dispersity (M_w/M_n) are given in Table-2.

Thermal studies: Thermogravimetric analysis curves shown the thermal behaviour of homopolymer, copolymers and terpolymer in Fig. 1. Which is analyzed on Perkin Elmer



Scheme-I: Synthesis of monomer [PANMI] and copolymers: [C₁PANMI] and [C₂PANMI]



Scheme-II: Synthesis of terpolymer: [T₁PANMI]

TABLE-1
FT-IR AND ¹H NMR SPECTRAL DATA OF PANMI, HPANMI, C₁PANMI, C₂PANMI AND T₁PANMI

Technique	PANMI	HPANMI	C ₁ PANMI	C ₂ PANMI	T ₁ PANMI	Characteristics
FT-IR (cm ⁻¹)	3300	3363	3359	3372	3355	N-H Stretch of amide
	1702	1713	1710	1714	1714	C=O Sym. & Asym. stretch of imide
	1666	-	-	-	-	C-C stretch of CH=CH
	1603	1603	1602	1601	1602	C=O Stretch of amide
	1372	1373	1396	1379	1392	C-N-C stret. of N – Subs. maleimide
	3095	3074	3073	3070	3071	C-H stretch of aromatic CH=CH
	1534	1515	1515	1516	1515	N=N stretch in aromatic
	1407, 1345	1444, 1344	1447, 1396	1445, 1344	1447, 1314	-NO ₂ Asym. And sym. Stretch
	836	836	838	836	837	P-substituted Ar
¹ H NMR (δ ppm)	730	741	753	751	752	Ortho- substituted Ar
	7.43, 7.19	7.91, 7.68	7.91, 7.06	7.93, 7.66	8.14, 7.91	Phenyl proton of <i>ortho</i> to N of imide
	7.20	7.19	7.53	7.68	7.73	Phenyl proton of <i>meta</i> to N of imide
	7.65	8.19	8.27	8.23	8.10	AzoSubs. Phenyl proton of <i>ortho</i> to N=N-C
	7.69	8.27	8.22	8.29	8.22	Azp Substituted Phenyl protons of <i>meta</i> to N=N-C
	-	-	11.89	11.76	10.73	-COOH
	7.07	-	-	-	-	(CH=CH)
	-	3.50	3.52	3.46	3.40	-[CH-CH] _n -
	10.05	10.07	10.08	10.09	10.09	-CONH

TABLE-2
DENSITY, INTRINSIC VISCOSITY, MOLECULAR WEIGHT OF HOMOPOLYMER, COPOLYMER AND TERPOLYMER

Polymer code	ρ (g/cm ³)	η (dl/g)	M _n	M _w	Poly dispersity index (PDI)
H-PANMI	0.5319	0.121	928.9	1104.8	1.189
C ₁ PANMI	0.9013	0.278	984.2	1255.9	1.276
C ₂ PANMI	0.8069	0.153	956.8	1175.1	1.228
T ₁ PANMI	0.9246	0.518	977.7	1313.7	1.343

TABLE-3
WEIGHT LOSS (%) OF H-PANMI, C₁PANMI, C₂PANMI AND T₁PANMI AT VARIOUS TEMPERATURE RANGE FROM THE TGA

Polymer code	Weight loss (%)					
	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C
H-PANMI	94.48	83.05	67.67	53.21	42.19	36.29
C ₁ PANMI	94.27	80.09	65.86	52.56	43.00	38.04
C ₂ PANMI	90.80	78.68	59.92	42.49	35.77	32.38
T ₁ PANMI	94.54	79.51	67.31	49.53	39.76	35.30

pyris1 TGA with thermal range of 30 to 1000 °C and analyzed accompanied by heating rate of 10 °C/min. in inert atmosphere of nitrogen. The results of percentage weight loss suffered from 200 to 700 °C at 100 intervals are shown in Table-3. All polymer decomposed by continuous degradation mechanism according to the resultant thermograms and shown excellent stability towards high temperature (Table-3). DSC analysis was also performed on NETZSCH DSC 204. The value of T_g for homopolymer, copolymers and terpolymer were summarized in Table-4. The T_g value also concluded the terpolymer having significance glass transition point with following flexibility in polymeric rigid spine due to mixing of vinyl acetate and thermal behaviour was maintained by the active participation of intermolecular hydrogen bonding.

A comparison of T_g of the present terpolymer [T₁PANMI] and copolymers [C₁PANMI], [C₂PANMI] showed significant observation in thermal behaviour. It was intimated that incorporation of synthesized N-substituted maleimide unit in vinyl acetate (VA) and acrylic acid (AA) has increased T_g value of comonomers (VA, AA) due to formation of H-bonding in polymer structures thus it was demonstrated a valuable changes in low temperature stable objects to revealed good thermal

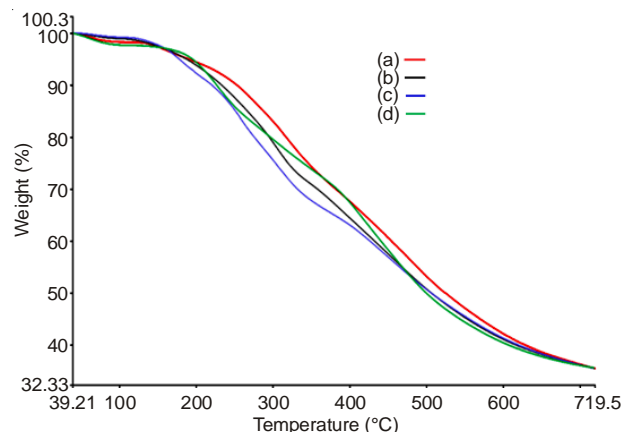


Fig. 1. TGA Thermograms of (a) H-PANMI (b) C₁PANMI (c) C₂PANMI (d) T₁PANMI

TABLE-4
THERMAL BEHAVIOUR OF H-PANMI, C₁PANMI, C₂PANMI AND T₁PANMI

Polymer code	H-PANMI	C ₁ PANMI	C ₂ PANMI	T ₁ PANMI
T _g (°C)	169.1	167	120.1	188.9
ΔCp* (J/g K)	1.806	1.302	0.270	0.153

stability and also create flexibility in highly rigid spine of maleimide polymers. Although homopolymer of maleimide monomer shown good T_g value and thermal susceptibility but that is exist in rigidity and to overcome this type of rigidity, vinyl acetate and acrylic acid used in homopolymer to enhanced flexibility. The equivalent T_g values of polymers were confirmed the establishment of “H-bonding” in co- and ter-polymers. That’s why, flexibility/softness of vinyl acetate and thermal property of maleimide collaborated and supported against individual drawbacks with help of “H-bonding” which is reflecting by acrylic acid to architect high performing copolymer and terpolymer comparatively.

Microbial activity: In sequence to explore biological activities of homopolymer, copolymers and terpolymer were evaluated against various microorganism such as *Escherichia aerogenes*, *Staphylococcus aureus* bacteria and *Aspergillus niger*, *Alternaria solani* fungi with DMSO as solvent with sample concentration was 500 µg/mL. Synthesized polymers revealed good antibacterial activity against used bacteria and fungi. The antimicrobial activity of homopolymer, copolymers and terpolymer were shown due to presence of heteroatom matrix in polymers (Table-5).

TABLE-5
MICROBIAL ACTIVITY OF H-PANMI
AND C₁PANMI, C₂PANMI AND T₁PANMI

Code	Zone of inhibition (mm)			
	Antibacterial activity		Antifungal activity	
	<i>E. aerogenes</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>A. solani</i>
H-PANMI	6	6.7	9	8.5
C ₁ -PANMI	10	10.8	16	13
C ₂ -PANMI	7	8	9	10
T ₁ -PANMI	14	11	15	18

Conclusion

Synthesis through free radical homopolymerization of H-PANMI, copolymerization of C₁PANMI, C₂PANMI and terpolymerization of T₁PANMI have been investigated. The characterization of homo-, co- and ter-polymers has been carried out through elemental analysis, FTIR, ¹H NMR spectral analysis, solubility test and density, viscosity measurement. The thermal properties were investigated by TGA and DSC. C₁PANMI, C₂PANMI and T₁PANMI exhibited good thermal stability and T_g value with sustain flexibility than their homopolymer due to the presence of secondary force “H-bonding” and polymers was degrade in continuation according thermograms. The synthesized all polymers showed good antimicrobial features, could be played significantly in concern applications.

REFERENCES

1. M.Jiang, N.Xu, C.Xiao and X.Han, *J. Macromol. Sci. Part B Phys.*, **53**, 1814 (2014).
2. B.L. Hiran and S.N. Paliwal, *J. Macromol. Sci. Part A Pure Appl. Chem.*, **46**, 713 (2009).
3. D. Jain, J. Maheshwari, N. Rathore and S.N. Paliwal, *Rasayan J. Chem.*, **5**, 445 (2012).
4. S.L. Oswal, N.N. Chapaneri and N.I. Malek, *Design. Monom. Polym.*, **10**, 487 (2007).
5. B. Wang, J.F. Hinton and P. Pulay, *J. Phys. Chem.*, **107**, 4683 (2003).
6. A. Omayu, S. Yoshioka and A. Matsumoto, *Macromol. Chem. Phys.*, **210**, 1210 (2009).
7. K. Backfolk, R. Holmes, P. Ihalainen, P. Sirviö, N. Triantafillopoulos and J. Peltonen, *Polym. Test.*, **26**, 1031 (2007).
8. A. Mbulu, *Mater. Sci.*, **23**, 9 (2008).
9. Q.H. Zhou, L. Ming, P. Yang and G. Yi, *Macromol. Theory Simul.*, **22**, 107 (2013).
10. I.A. Mohammed and A. Mustapha, *Molecules*, **15**, 7498 (2010).