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COPOLYMERIZATION AND CHARACTERIZATION OF ETHYLENE GLYCOL ALLENYL METHYL ETHER WITH N-VINYL PYRROLIDONE

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Key Words: Allenyl Ethers, Copolymerization, Reactivity Ratios, Thermal Degradation

ABSTRACT

The radical copolymerization of monoethylene glycol allenyl methyl ether (MEGA), with N-vinyl pyrrolidone (Vp) were investigated at various compositions using AIBN as initiator at 60°C. The composition of the copolymers were characterized by ^{1}H NMR, IR and GPC techniques.

Values of reactivity ratios were determined using NMR methods, r_1 (MEGA) = 0.41 ± 0.05 and r_2 (VP) =0.765 ± 0.08 calculated. Thermal stability and degradation behavior of the polymers were examined using TG/DTG methods. The thermal stability of the copolymers were intermediate between those of the two homopolymers, and appear to degrade in two stages. The first stage resulting from decomposition of C-O bonds of the side chain and the C-C bonds β to double bonds of PMEGA units. The second stage resulted from decomposition of the pyrrolidone ring of PVP units.

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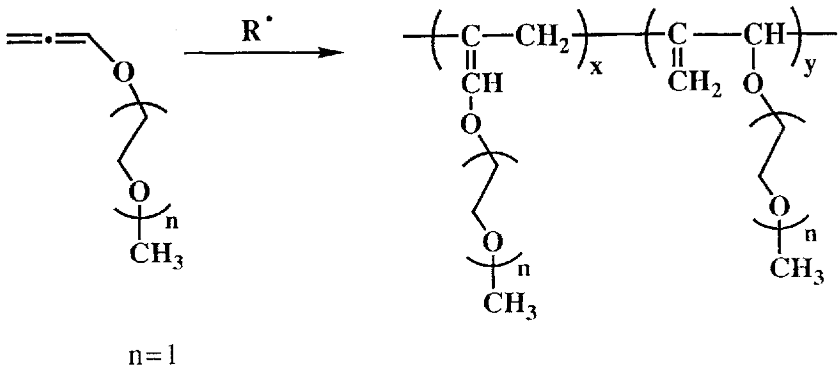


SCHEME 1

INTRODUCTION

Allenyl ether polymers, which have hydrophilic oligo (oxyethylene) side chains are a novel class of polymers that contain reactive vinylidene moieties in their main chains [1]. Such polymers are important for many applications such as phase transfer catalysts, ionic conductive polymers, supports for enzyme and purification of proteins [2].

Radical polymerization of vinyl ether is usually difficult due to high chain transfer constant of the propagating radical [3-5]. The propagation end of the allenyl ethers may be stabilized by the allylic structure which does not exist in vinyl ethers. The stabilized allylic radical may have a lower chain transfer constant.

Recently, we have reported on radical polymerization and properties of allenyl ethers (n = 1-3), which bear oligo (oxyethylene) chains, as shown in Scheme 1. Synthesis and copolymerization of allenyl ether macromonomers with styrene have been discussed elsewhere [6-7]. In the present work, attempts were made to study the radical copolymerizability of ethylene glycol allenyl methyl ether (n=1) with N-vinyl pyrrolidone and to characterize the obtained polymers by IR, NMR and GPC techniques. The thermal stability of the polymers have been assessed by TG/DTG measurements.

EXPERIMENTAL

Materials

Mono(ethylene glycol) allenyl methyl ether (MEGA), was prepared as previously reported. N-vinyl pyrrolidone (VP), (Aldrich), was dried over CaH_2 and

TABLE 1. Experimental Details of the Copolymerization of MEGA with VP

Sample	MEGA g (mmol)	VP g(mmol)	Feed ratio MEGA :VP	Mole fraction of MEGA in feed
MEGA-VP 21	0.288 (2mmol)	0.111 (1mmol)	2:1	0.66
MEGA-VP 11	1.44 (1mmol)	0.111 (1mmol)	1:1	0.50
MEGA-VP 12	0.144(1mmol)	0.222(2mmol)	1:2	0.33
MEGA-VP 13	0.144(1mmol)	0.333(3mmol)	1:3	0.25

distilled under vacuum. 2,2'-azobisisobutyronitrile (AIBN) was purified by the usual methods [8]. All the other chemicals used were of analytical grade.

Chemical Preparation of Homopolymers

Poly(ethylene glycol) allenyl methyl ether (PMEGA) was synthesized in benzene with AIBN (3 mol%) as initiator at 60°C. The polymer was precipitated in hexane, dried under vacuum. Poly(vinyl pyrrolidone) (PVP), was prepared by the same procedure and dried under vacuum for 12 hours.

Preparation of Copolymers

Four poly[(ethylene glycol) allenyl methyl ether-co-vinyl pyrrolidone] (MEGA-VP), with different comonomer feed ratios, were synthesized chemically in an analogous manner to homopolymer at reaction time 2 hours. The experimental details are provided in Table 1.

Infrared Spectroscopy

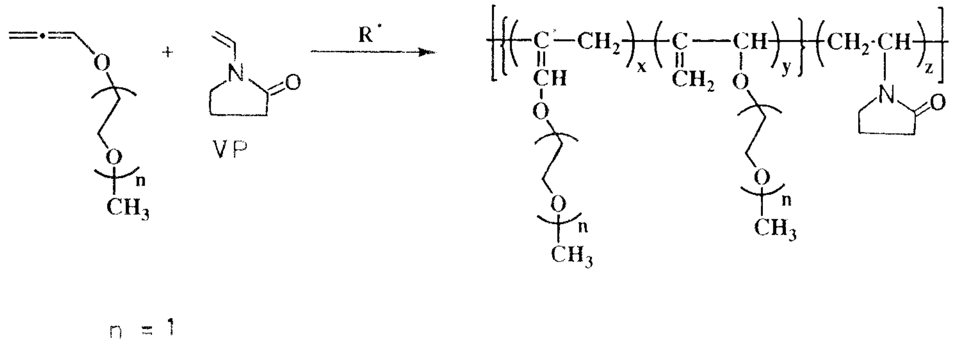
IR spectra of the polymers were recorded on a JASCO FT/IR 5300 Spectrometer. The spectra were measured at room temperature (25°C), with the polymer samples dispersed in KBr disk pellets.

Nuclear Magnetic Resonance Spectroscopy

^1H NMR spectra recorded in $CDCl_3$ on a JEOL EX-90 instrument (90 MHz, tetramethylsilane as an internal standard).

Gel-Permeation Chromatography

GPC analyses were carried out on a TOSOH CCPD (TSK gel G 4000, THF as an eluent) on the basis of standard polystyrene samples.



SCHEME 2

Thermal Methods of Analyses

Thermogravimetric (TG), and derivative thermogravimetric (DTG) analyses of polymers were performed on a Du Pont 950 thermobalance. 10 mg samples were heated from 50 to 550°C at 10 deg/min^{-1} in a dynamic nitrogen atmosphere (70 ml/min).

RESULTS AND DISCUSSION

Substituted allenes can be expected to be attractive monomers, since they might produce polymers with reactive exomethylene units in their main chain upon 1,2- or 2,3- polymerization. The radical copolymerization of MEGA and VP, using AIBN may be represented schematically according to Scheme 2.

The resulting copolymers were white, rubbery-like materials, soluble in water and alcohols. The $\overline{M}_n$ values of copolymers determined from GPC were of 2800, 2600, 1700 and 1500 at 0.66, 0.5, 0.33 and 0.25 mole fraction of monoethylene glycol allenyl methyl ether in feed.

The IR spectra of PVP, PMEGA, and MEGA-VP11 copolymers (taken as typical examples of copolymers), are shown in Figure 1. The copolymers sample showed that there is no allenyl absorption band at 1952 cm^{-1} of MEGA unit, and the olefinic absorption band $\nu_{C=C}$ at 1668 cm^{-1} can be observed in the spectra. The chain of the copolymer are built from VP units (3435, 2967, 1705, 1425, 1060, 850 cm^{-1}) and MEGA units (3043, 2928, 2876, 1716, 1668, 1097 cm^{-1}).

Figure 2 shows the ^{1}H NMR spectrum for the MEGA-VP11 copolymers, whose composition was taken as a typical example. The composition of copolymers

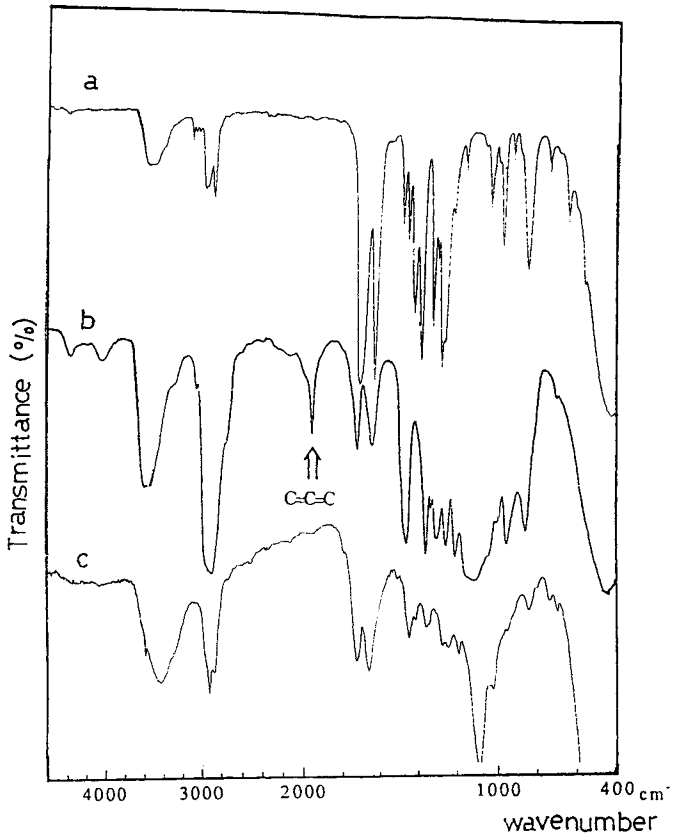


Figure 1. IR Spectra of (a) PVP, (b) MEGA, and (c) MEGA-VP11 Copolymer.

were determined by comparing the integrals of four protons in positions three and four of the pyrrolidone ring and the methylene groups of the main chain at 1-2.6 ppm with those of oxyethylene side chains at 3.3 ppm (-OCH_3,s); at 3-7 ppm (-O-CH_2-CH_2O-br) and at 3.4 ppm (N-CH_2-,br). Protons of the copolymer at 4.3-5.2 ppm (O-CH, C=CH_2, br) and at 5.3-6.2 ppm (C=CH-O, br) shows very small NMR peaks, due to the produced polymers were composed of 2, 3- and 1, 2-polymerized units in the ratio of X:Y = 65:35- 50:50 [1, 7].

The integral values of ^1H NMR peaks were conveniently used for the determination of the copolymer compositions. Knowing the molar ratio of the monomer in the comonomer mixtures and in different copolymers, the composition diagram can be represented as in Figure 3. Reactivity ratios can be determined using

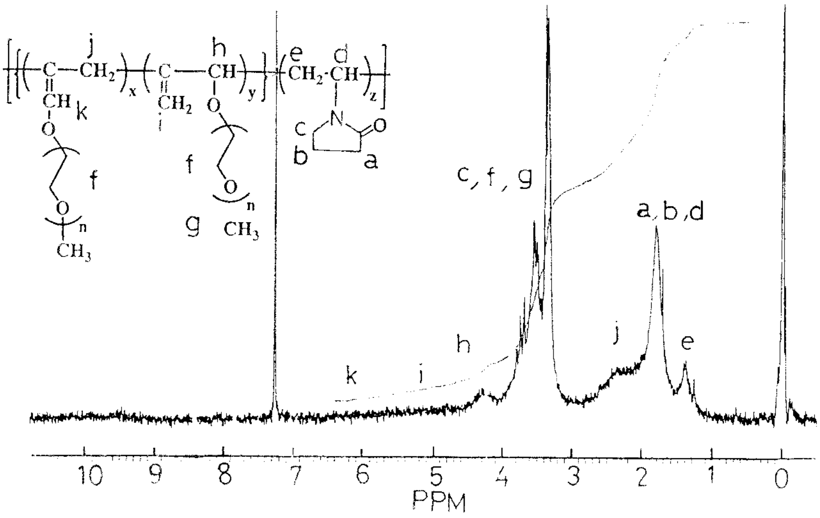


Figure 2. ^{1}H NMR Spectrum of copolymer of N-vinyl pyrrolidone and MEGA, [VP-MEG21].

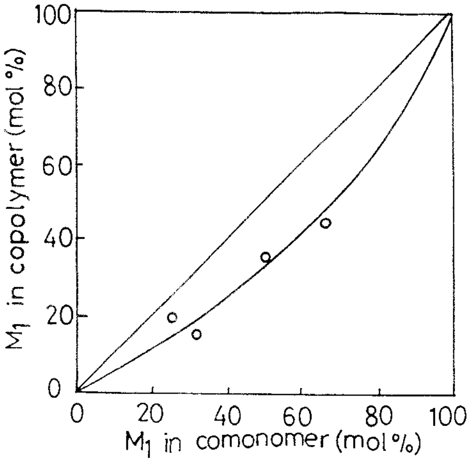


Figure 3. Composition diagram of the copolymerization of MEGA [M_1] and VP [M_2].

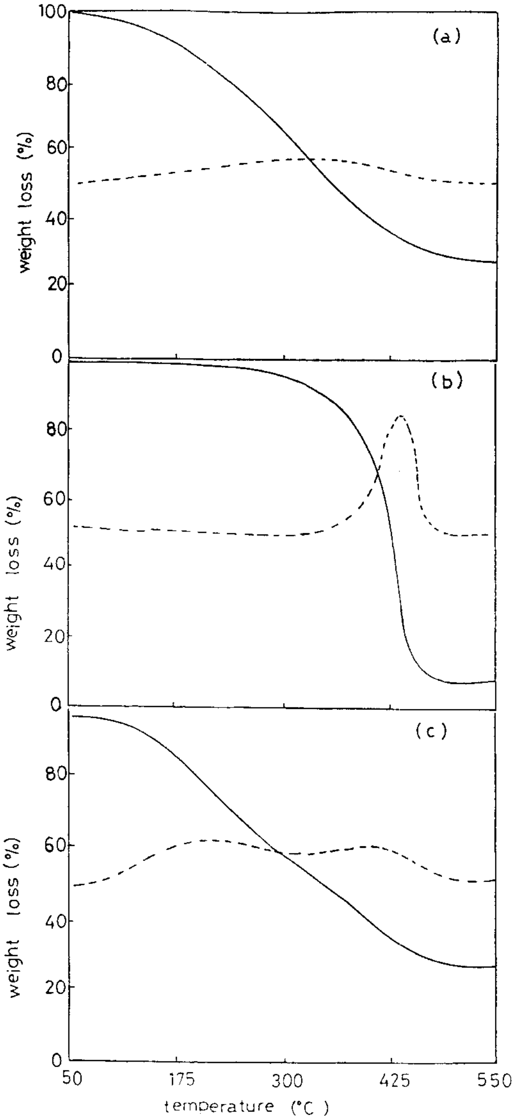


Figure 4. TG [-] and DTG [--] thermal curves of: (a) PMEGA; (b) PVP; (c) MEGA-VP21 copolymer.

the Kelen-Tudos method. The reactivity ratio values for MEGA-VP copolymer r_1 (MEGA) = 0.41 ± 0.05 and r_2 (VP) = 0.765 ± 0.08. TG and DTG thermograms for the PMEGA, PVP, and MEGA-VP21 polymers are shown in Figure 4. The curves show that there is only one degradation step in the case of homopolymers, and two steps in the case of copolymers.

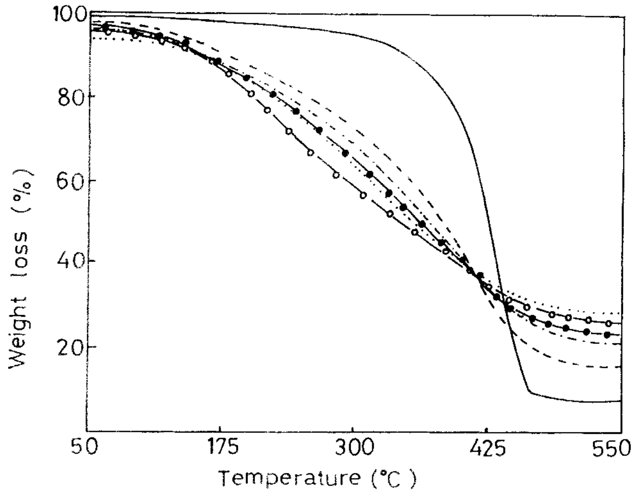


Figure 5. TG weight loss curves of MEGA, VP and MEGA-VP copolymers: [-] PVP; [--] MEGA-VP13; [-.-] MEGA-VP12; [-o-o-] MEGA-VP11; [-●-●-] MEGA-VP21, [...] PMEGA.

The thermal degradation behavior of poly(ethylene glycol) allenyl methyl ether, as shown in TG and DTG (Figure 4a), exhibits low thermal stability. It degrades early at about 95°C and degrades continuously until it reaches to about 480°C with a high rate of weight loss. The maximum temperature of degradation was about 340°C, with a weight loss 54% as indicated from the DTG broad curve.

The low thermal stability of PMEGA can easily be attributed to decomposition of C-O bonds at the side chains which are adjacent to the main chain of the polymer, and also to the thermal instability of C-C bonds β to double bonds [10]. A similar behavior was observed by Casta *et al.* [11], for the degradation of poly(ethyleneoxide) and its metal complexes. The scission in alkoxy radical, which involves a C-O bonds, is characterized by a low energy [12-14].

Figure 4b shows the TG/DTG curves for PVP. The thermal behavior of PVP was well known in the literature [15-17]. It shows a high thermal stability, and exhibits only one decomposition region. It degrades at about 400°C with weight loss about 10%, which may be due to evaporation of solvents and moisture, and ends at about 460°C with weight loss about 93%. The T_{max} of decomposition was 432°C with weight loss about 71%.

The TG and DTG curves for MEGA-VP21 copolymer are shown in Figure 4c. Its thermal behavior was intermediate between those of the two homo-

TABLE 2. TG Data for the Homopolymers and Copolymers

Polymer	Volatilization temperature °C	First stage		Second stage		wt% remaining at 500 °C
		T_{max} °C	wt loss%	T_{max} °C	wt loss %	
PMEGA	95	-	-	340	54	31
MEGA-VP 21	118	212	64	405	64	27
MEGA-VP 11	124	220	63	410	63	25
MEGA-VP 12	130	237	62	412	62	23
MEGA-VP 13	140	276	61	413	61	18
PVP	400	-	-	432	56	8

polymers. It degraded in two steps; the first one starts at about 118°C and ended at about 270°C with weight loss about 47% and the T_{max} of decomposition was 212°C. The second stage followed the first stage and ended at about 450°C with weight loss about 75%. The DTG curves of this stage exhibits a maximum at 405°C. At 520°C, a plateau is observed in TG curve as dw/dt is zero.

The thermal behavior, with different ratios of copolymers, have been compared with their parent homopolymers PMEGA and PVP, as shown in Figure 5.

The volatilization temperatures of copolymers begins at temperature range from 118-140°C. So, the first stage of decomposition has T_{max} from 212-275°C, and ends at temperature from 260-325°C. The second stage which followed the first stage ends at temperature from 430-470°C. Table 2 presents the percentage of weight loss for all polymers and the maximum rate of decomposition determined from the DTG curves.

These data indicate that the behavior of the copolymers is a hybrid of those of their homopolymers. Therefore, the enhancement of the thermal degradation of the copolymers can result from the stabilizing effect of the pyrrolidone ring on the copolymer structure [18-19]. A similar study of the thermal stability of 4-vinyl pyridine-methyl methacrylate copolymers by Khariou *et al.* [20], suggested that the thermal stability of copolymers result from the pyridine ring.

CONCLUSION

The copolymers of MEGA with VP were synthesized and characterized by different methods. From IR and ^{1}H NMR, the structure of the copolymers and the reactivity ratios were determined. Enhancement of the thermal stability of poly(ethylene glycol) allenyl methyl ether is achieved by its copolymerization with N-vinyl pyrrolidone. The TG curves of copolymers may be divided into two regions, the first resulting from the decomposition of low thermal stability C-O bonds of the side chain and the thermal instability of C-C bonds β to double bonds of the PMEGA units. The second, was attributed to the decomposition of the pyrrolidone ring of the PVP units.

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