Organotin polymers–V. Binary and ternary copolymerization reactions of tributyltin acrylate and methacrylate with vinyl acetate and *N*-vinylpyrrolidone

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Copolymerization reactions were carried out in solution at 70°C in the presence of a free radical initiator, and the copolymer composition in each case was determined from tin analysis. The monomer reactivity ratios for the copolymerization reactions of tributyltin acrylate with vinyl acetate and *N*-vinylpyrrolidone were found to be: $r_1=2.567$, $r_2=0.006$ and $r_1=0.513$, $r_2=0.610$, respectively. Also, the copolymerization parameters of tributyltin methacrylate with vinyl acetate and *N*-vinylpyrrolidone were: $r_1=4.408$, $r_2=0.017$ and $r_1=3.160$, $r_2=0.438$, respectively. Four selected terpolymer feed compositions involving tributyltin acrylate or methacrylate with vinyl acetate or methyl methacrylate and *N*-vinylpyrrolidone or acrylonitrile, were polymerized to low conversion and the terpolymer composition in each case was calculated from tin and nitrogen analyses. The variations of terpolymer composition with conversion fit the experimental results over a wide range of conversion. The structure of the prepared co- and terpolymers was investigated by i.r. spectroscopy.

INTRODUCTION

Organotin polymers are gaining extensive use as antibacterial, antifungal and antifouling coatings. Copolymers containing trialkyltin moieties chemically attached on their backbones were developed by Montemarano and Dyckman[1] to produce long-lived, low pollution risk and film-forming resinous coating materials. Atherton *et al.*[2] reported that the use of hydrolyzable organometallic binders allows the incorporation of higher proportions of toxin and better control of toxin release. Optimal application properties for such copolymers could be achieved through studies of their copolymerization parameters. However, little work has been done on this relatively novel subject. In our previous studies[3–6], the monomer reactivity ratios of tributyltin acrylate or methacrylate with the alkyl esters of methacrylic or acrylic acids as well as acrylonitrile, styrene or allyl methacrylate have been obtained. The aim of the present work is to study the copolymerization reactions of tributyltin acrylate and methacrylate with both vinyl acetate and *N*-vinylpyrrolidone. Also, the terpolymerization reactions of four systems involving tributyltin acrylate or methacrylate, with vinyl acetate or methyl methacrylate, and acrylonitrile or *N*-vinylpyrrolidone, were studied to check the validity of the determined reactivity ratios. It is also aimed to follow the variation of terpolymer composition at various conversions.

EXPERIMENTAL

The tin-containing monomers, tributyltin acrylate (BTA) and tributyltin methacrylate (BTMA) were prepared through the reaction of acrylic or methacrylic acids with tri-n-butyltin oxide according to the method of Cummins and Dunn[7]. Vinyl acetate (VA), *N*-vinylpyrrolidone (NVP), methyl methacrylate (MMA), and acrylonitrile (AN) monomers (E. Merck, Darmstadt, products) were purified by distillation under reduced pressure and the middle fractions retained for use.

Copolymers from BTA and BTMA with VA and NVP, were obtained by solution polymerization in toluene (3 mol^{-1}) at 70°C, in presence of 1 mol% azo-bis-isobutyronitrile as a free radical initiator, according to the method previously described[4]. Copolymers produced from NVP with both organotin monomers were purified by reprecipitation from petroleum ether, while copolymers containing VA were precipitated from 90% methanol, and all samples obtained in each case were washed several times, dried and weighed. Overall conversion, calculated from the weight of polymer obtained from a known amount of comonomer feed, was limited to less than 10% conversion in each case.

Azeotropic composition and some selected terpolymer compositions were similarly prepared over a wide range of conversion. Copolymer and terpolymer samples were analyzed for their tin content by the method of Gilman and Rosenberg[8], and the nitrogen contents were determined by a modified Kjeldahl method. The infra-red spectra were run on a Beckman 4220 spectrophotometer using the thin-film technique.

RESULTS AND DISCUSSION

The copolymerization parameters for BTA–VA, BTA–NVP, BTMA–VA and BTMA–NVP systems were determined from the feed composition–copolymer com-

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Table 1 Monomer reactivity ratios for copolymerization reactions of BTA and BTMA with VA and NVP

	Fineman–Ross Method			Kelen–Tüdös Method			
M_1–M_2	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2	α
BTA–VA	2.567 ± 0.046	0.006 ± 0.006	0.0154	2.624 ± 0.201	0.013 ± 0.006	0.0341	0.0946
BTA–NVP	0.513 ± 0.008	0.610 ± 0.020	0.3129	0.507 ± 0.025	0.604 ± 0.026	0.306	1.1767
BTMA–VA	4.408 ± 0.057	0.017 ± 0.012	0.0749	4.615 ± 0.370	0.037 ± 0.006	0.170	0.0436
BTMA–NVP	3.160 ± 0.202	0.438 ± 0.057	1.3840	3.147 ± 0.291	0.435 ± 0.055	1.368	0.2267

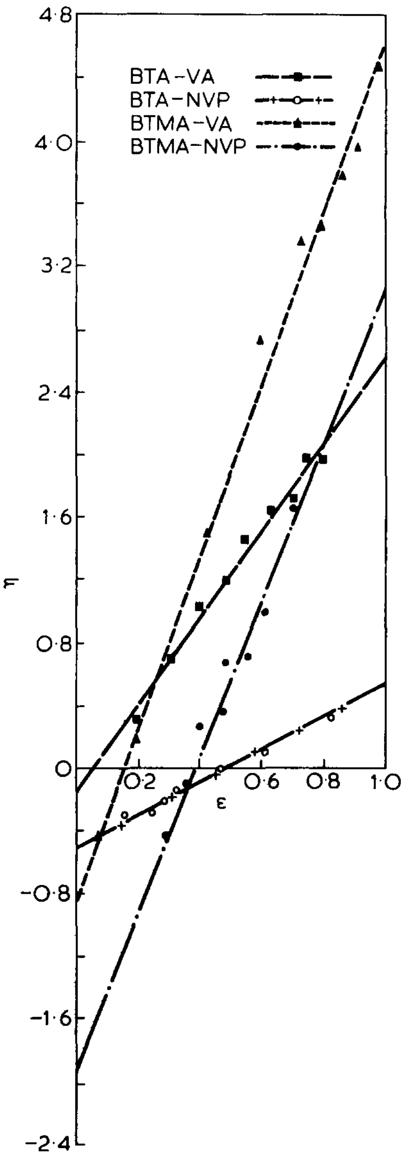

Figure 1 Kelen–Tüdös plots for copolymerization reactions of BTA and BTMA with VA and NVP. $\eta = a(b-1)/\alpha b + a^2$ and $\epsilon = a^2/\alpha b + a^2$ (where a and b are the comonomer feed and copolymer compositions, respectively, in molar ratio)

position relationship according to the Fineman–Ross[9] and Kelen–Tüdös[10] methods. *Table 1* illustrates the monomer reactivity ratios for the four systems, and the standard deviations of the results calculated by regression analysis. *Figures 1* and *2* show the Kelen–Tudos plots and the copolymerization composition curves for the systems studied, respectively. *Table 1* shows that the monomer reactivity ratio values of the organotin monomers (r_1) are much greater than the r_2 values of VA and NVP for BTA–VA, BTMA–VA and BTMA–NVP systems. However, the r_1 and r_2 values for BTA–NVP system are both less than unity, indicating that the copolymer would be expected to contain a significant amount of alternating monomer unit sequences along the polymer chain and the copolymerization reaction of this system should have an azeotropic composition. *Figure 2* shows the copolymerization composition curve for BTA–NVP system crossing the line representing $F_1 = f_1$, as expected, at 0.44 mol fraction. Therefore the azeotropic comonomer composition for this system (BTA–NVP, 0.44:0.56) was polymerized to several conversions covering a wide range, as illustrated in *Figure 3*, which shows the relation between yield of copolymer *versus* time. *Figure 4* shows the tin content of each copolymer sample as a function of conversion and indicates that the copolymer composition remains constant regardless of conversion. The tin content of the copolymer samples gave a mean value of 23.75% for the azeotropic composition of BTA–NVP system. The copolymerization reaction of this azeotropic system was found to be a vigorous exothermic reaction and reached 95% conversion within 40 min (*Figure 3*).

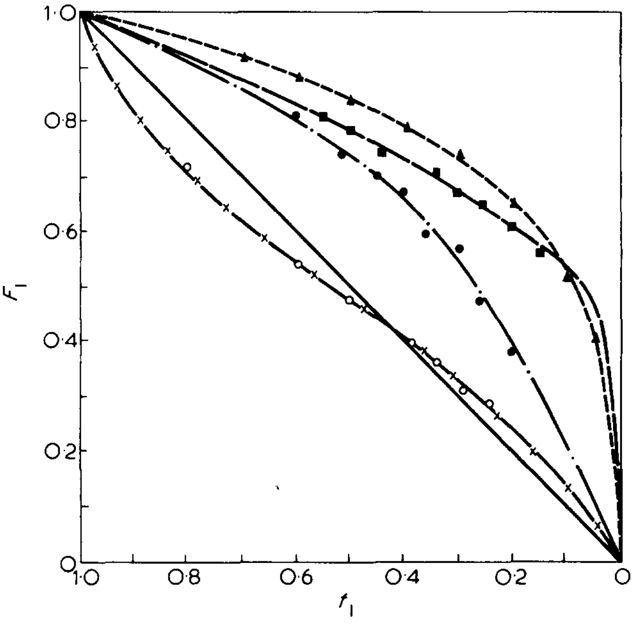

Figure 2 Composition curves for polymerization reactions of BTA and BTMA with VA and NVP (f_1 and F_1 are mol fractions of the organotin monomer in the feed and copolymer, respectively)

Molecular heterogeneity has a direct effect on the physical properties of polymers. We studied the changes in terpolymer composition with conversion for VA–BTA–NVP, VA–BTA–AN, VA–BTMA–AN and MMA–BTMA–NVP systems. The presence of tin and nitrogen in these terpolymer compositions facilitates the determination of the terpolymer composition. The feed compositions of the four systems were selected to contain larger amounts of the more reactive monomers to ensure uniformity of terpolymer composition over a wide range of conversion. These feed compositions (*Table 2*) were polymerized to different levels of conversion as shown in *Figure 3* which illustrates the percent conversion as a function of time. The terpolymer composition of each sample was determined through tin and nitrogen analyses. The results of tin and nitrogen analyses for the four terpolymer systems polymerized to low conversions (less than 10%), are shown in *Table 2*. The instantaneous terpolymer composition for each feed was calculated by using the terpolymer composition equation in the form proposed by Khan and Horowitz[11]. The calculation of the terpolymer composition requires the monomer reactivity ratios of the individual two-component systems. The reactivity ratios used for calculating the terpolymer composition of each system, determined in the present investigation, our previous studies and the literature values, are illustrated in *Table 3*. The calculated terpolymer compositions are in good agreement with the experimental results based on tin and nitrogen analyses as shown in *Table 2*, which proves the accuracy of the determined reactivity ratios used for predicting the terpolymer composition.

Predictions of both the instantaneous and average terpolymer compositions were obtained at each level of conversion for each system by integration of the terpolymer composition equation[14], assuming that the polymer composition is constant within 10% interval. The variation of terpolymer composition with conversion for the four systems studied is shown in *Figures 5–8*, which indicate that the results of the average terpolymer compositions obtained from the analysis of the four systems at different levels of conversion are in good agreement with the predicted values. The variation of the instantaneous terpolymer composition with conversion for VA–BTA–NVP system (*Figure 5*) shows that both BTA and NVP were completely consumed at 86% and 92% conversions respectively, followed by VA homopolymer. Also, for VA–BTA–AN system (*Figure 6*) both AN and BTA disappeared at 90% and 92% conversions respectively, followed by VA homopolymer. For VA–BTMA–AN system, *Figure 7* shows that both BTMA and AN were completely gone at 94% conversion, and that molecular homogeneity

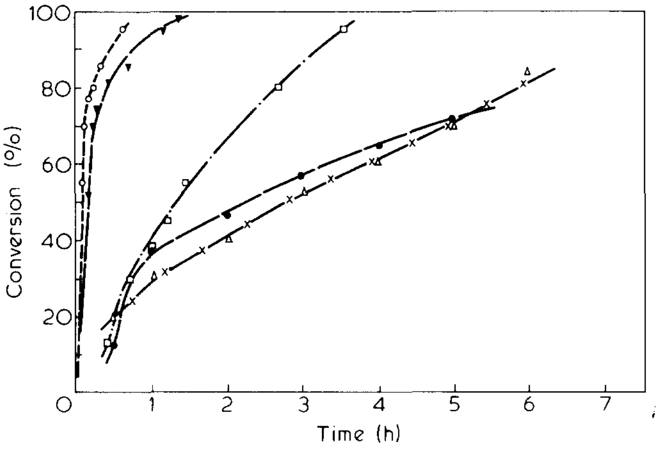

Figure 3 Percent conversion *versus* time for: BTA–NVP azeotropic copolymer (— — —○— — —), VA–BTA–NVP terpolymer (—▲—), VA–BTA–AN terpolymer (—●—), VA–BTMA–AN terpolymer (— x △ x —) and MMA–BTMA–NVP terpolymer (— . □ . —)

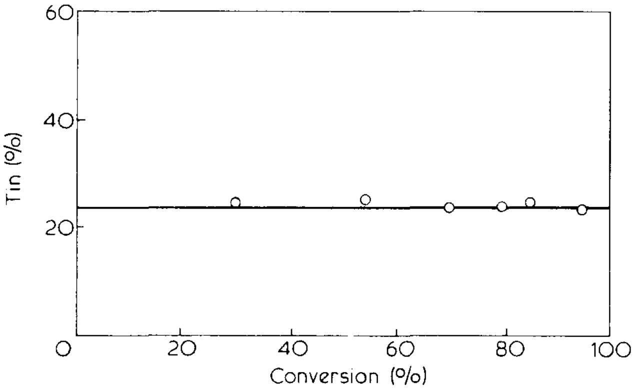

Figure 4 Tin percent as a function of conversion for azeotropic copolymerization of BTA–NVP system

Table 2 Initial terpolymer compositions from tin and nitrogen analyses

System	Feed (mol %)	Sn %	N %	Terpolymer composition (mol %) Found	Calculated
VA	21.95	25.00	2.73	6.73	7.17
BTA	39.45			48.36	47.97
NVP	38.60			44.91	44.86
VA	15.05	23.95	6.45	4.16	3.39
BTA	29.85			29.14	28.90
AN	55.10			66.70	67.71
VA	10.00	28.05	2.80	2.11	1.60
BTMA	50.05			52.96	52.96
AN	39.95			44.93	45.44
MMA	54.52	18.44	0.475	66.93	67.95
BTMA	24.63			27.17	26.58
NVP	20.85			5.90	5.47

Table 3 Monomer reactivity ratios used in determining various terpolymer compositions

	Monomer reactivity ratios					
M_1–M_2–M_3	r_{12}	r_{21}	r_{23}	r_{32}	r_{13}	r_{31}
VA–BTA–NVP	0.006	2.567(*)	0.513	0.610(*)	0.237	2.280(11)
VA–BTA–AN	0.006	2.567(*)	0.243	1.008(5)	0.05	4.20(12)
VA–BTMA–AN	0.017	4.408(*)	0.465	0.467(4)	0.05	4.20(12)
MMA–BTMA–NVP	1.004	0.789(3)	3.160	0.438(*)	4.60	0.02(13)

(*) Present study (*Table 1*)

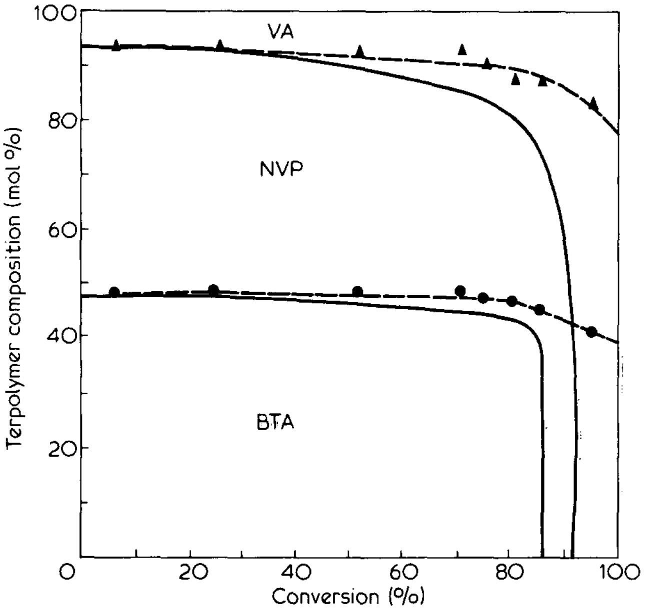

Figure 5 Terpolymer composition as a function of conversion for VA–BTA–NVP system, lines represent predicted values of instantaneous (——) and average (— — —) compositions, and points from experimental analysis (● = BTA and ▲ = BTA + NVP)

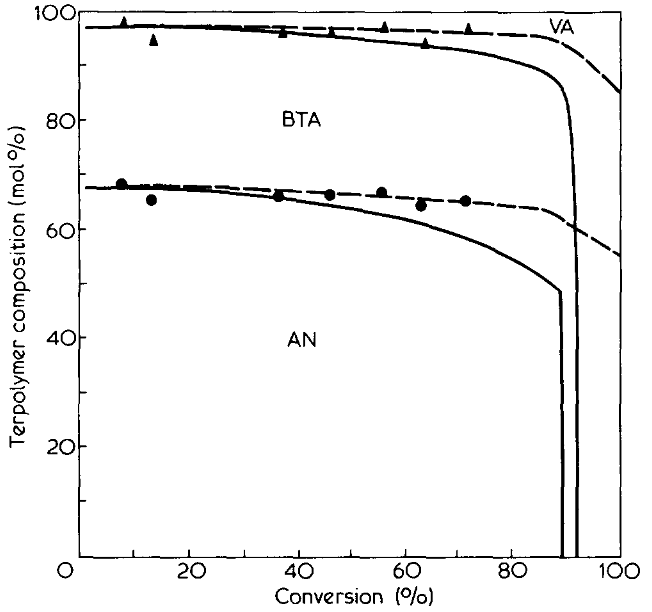

Figure 6 Terpolymer composition as a function of conversion for NA–BTA–AN system, lines represent predicted values of instantaneous (——) and average (— — —) compositions, and points from experimental analysis (● = AN and ▲ = AN + BTA)

for this system could be achieved up to 90% conversion. *Figure 8* shows that both MMA and BTMA had disappeared at 86% and 92% conversions for MMA–BTMA–NVP system.

Organotin polymers obtained from the studied binary and ternary systems are clear, transparent, soluble materials suitable for film formation. Copolymers produced from the copolymerization reactions of vinyl acetate are hard rubbery products, while all other co- and terpolymers are solids.

The structures of the prepared organotin polymers were investigated by infra-red spectroscopy. *Figure 10* shows the i.r. spectra of BTA–NVP azeotropic copolymer as well as VA–BTA–NVP and VA–BTMA–AN terpolymers, which indicate that these spectra are quite similar in the region 400–1200 cm^{-1}. The i.r. spectrum of BTA–NVP copolymer shows two strong bands at 1655 and 1690 cm^{-1}, characteristic for the stretching frequencies of the carboxylate carbonyl group of BTA and the carbonyl group of NVP, respectively. The i.r. spectrum of VA–

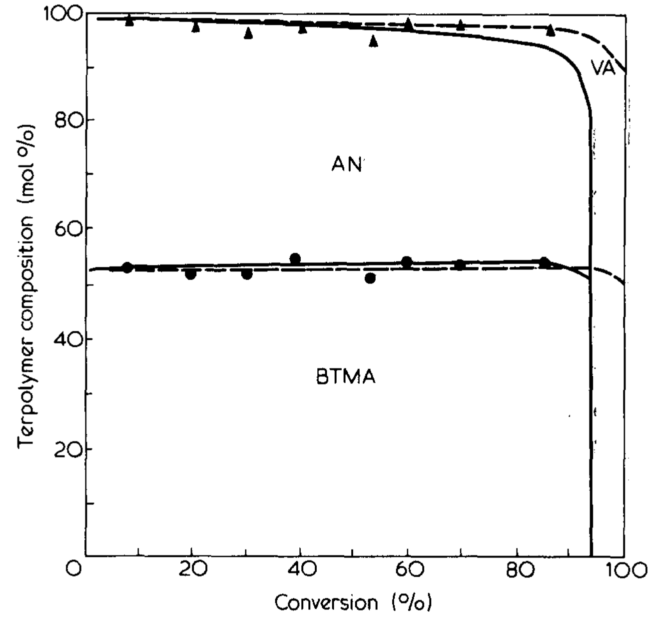

Figure 7 Terpolymer composition as a function of conversion for VA–BTMA–AN system, lines represent predicted values of instantaneous (——) and average (— — —) compositions, and points from experimental analysis (● = BTMA and ▲ = BTMA + AN)

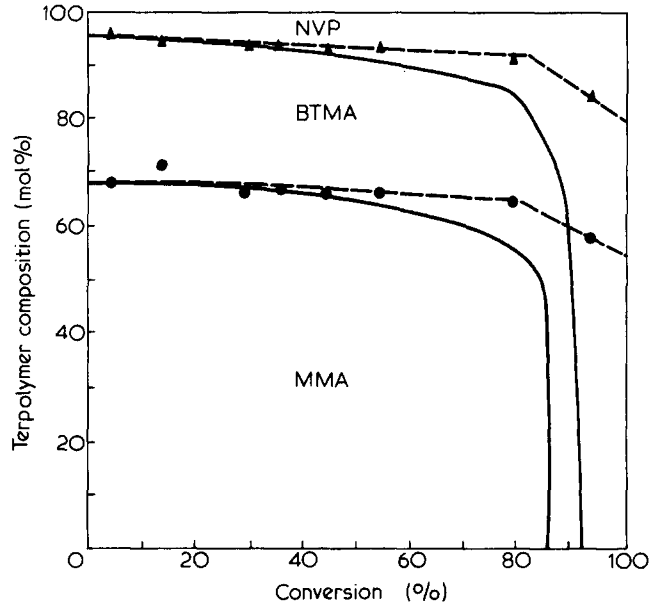

Figure 8 Terpolymer composition as a function of conversion for MMA–BTMA–NVP system, lines represent predicted values of instantaneous (——) and average (— — —) compositions, and points from experimental analysis (● = MMA and ▲ = MMA + BTDA)

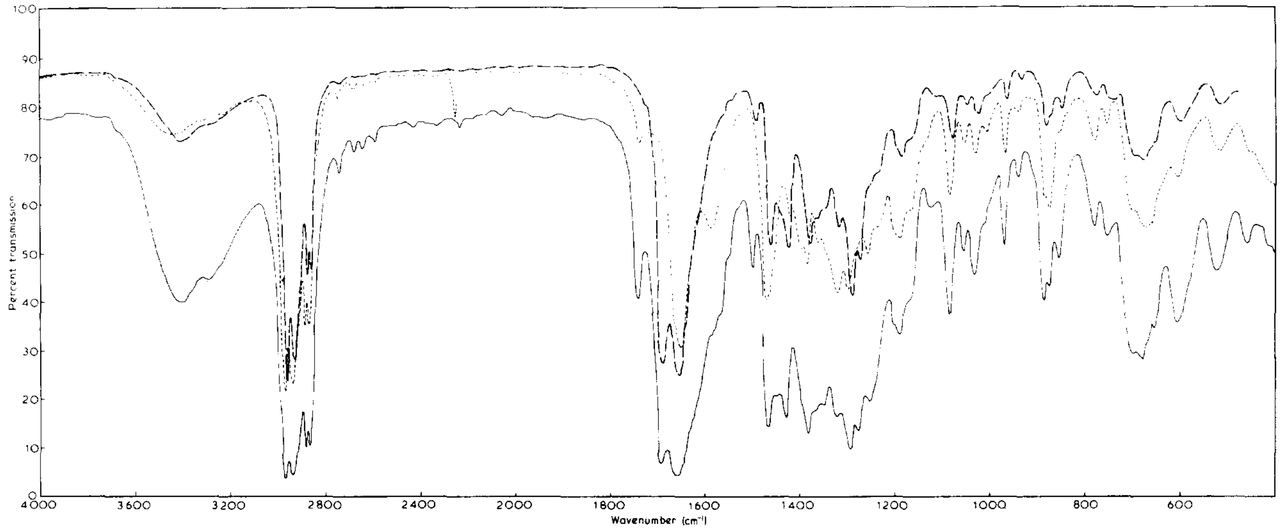

Figure 9 Infra-red spectra for: BTA–NVP copolymer (— — —), VA–BTAANVP terpolymer (——) and VA–BTMA–AN terpolymer (– – –)

BTA–NVP terpolymer shows three carbonyl bands at 1655, 1690 and 1740 cm^{-1} due to BTA, NVP and VA respectively, while the i.r. spectrum of VA–BTMA–AN terpolymer shows two carbonyl bands at 1650 and at 1740 cm^{-1} due to BTMA and VA respectively, and a band at 2240 cm^{-1} characteristic for the $-C{\equiv}N$ group of AN.

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