

# Acrylic-Functional Aminocarboxylic Acids and Derivatives as Components of Pressure-Sensitive Adhesives

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## Synopsis

High-performance thermoplastic pressure-sensitive adhesives have been prepared by copolymerization of *N*-acryloylamino acids and acid derivatives with long-chain alkyl acrylate esters. A comparative study with equivalent copolymers made from conventional polar comonomers and long-chain alkyl acrylate esters has shown that the *N*-acryloylamino acids and derivatives impart generally higher levels of tack, adhesion, and cohesion than their conventional counterparts.

## INTRODUCTION

Homopolymers of long-chain alkyl acrylates are quite tacky but lack the necessary cohesive strength to function as pressure-sensitive adhesives with well-balanced properties. Ulrich<sup>1</sup> discovered that cohesive integrity could be improved by copolymerizing with the long-chain alkyl acrylate esters monomers that contain functional groups capable of interpolymeric dipole-dipole or hydrogen-bonding interactions. Thus iso-amyl acrylate, iso-octyl acrylate, and the like were copolymerized with such polar monomers as acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, and acrylonitrile to ultimately prepare tapes having a proper balance of properties.

The present study was undertaken to assess the effectiveness of the various polar functional groups for improving the cohesive strength of the copolymer while maintaining the "tackiness" necessary to produce adequate adhesion. In connection with this study, we investigated a class of polar comonomers, the *N*-acryloylamino acids, that have previously been unreported as components of pressure-sensitive adhesives and were found to function as excellent monomers for that purpose.

## EXPERIMENTAL

All melting points were uncorrected. Viscosities were measured at 22°C using a Brookfield viscometer. Glass transition temperatures were recorded as the mean of the range in temperatures observed for two trials measured using a DuPont differential thermal analyzer, model 900, with programmed heating and cooling rates of 30°C/min. Gel-permeation chromatography was performed using a Waters gel-permeation chromatograph, model 200, with columns containing 10<sup>3</sup>–10<sup>7</sup>-Å pore sizes. The copolymer sample was first treated with di-

TABLE I  
*N*-Acryloylamino Acids Prepared

<i>N</i> -Acryloylamino acid <sup>a</sup>	Melting range, °C		Ref.
<i>N</i> -Acryloylglycine	127.5–129.5		4
<i>N</i> -Methacryloylglycine	104–105.5		5
<i>N</i> -Acryloyl- <i>N</i> -methylglycine	109.5–111		—
<i>N</i> -Acryloyl- <i>N</i> -(β-cyanoethyl)glycine	103–104		—
<i>N</i> -Acryloyl-L-proline	116–117		—
<i>N</i> -Acryloylalanine	127.5–129.5		6
<i>N</i> -Acryloylmethylalanine	185–186.5		7
<i>N</i> -Methacryloylmethylalanine	160–162		7
<i>N</i> -Acryloylnorleucine	100–102.5		—
<i>N</i> -Acryloylphenylalanine	121.5–123		6
<i>N</i> -Acryloylmethionine	93.5–95		—
<i>N</i> -Acryloylaspartic acid	157.5–158(d)		—
<i>N</i> -Acryloylasparagine	Polymerized		—
<i>N</i> -Acryloyl-β-alanine	96.5–99		8
<i>N</i> -Acryloyl-4-aminobutyric acid	98.5–100.5		8
<i>N</i> -Acryloyl-5-aminovaleric acid	92–94.5		—
<hr/>			
<i>N</i> -Acryloylamino acid derivatives <sup>a</sup>	Melting range, °C	Boiling range, °C/Torr	Ref.
<i>N</i> -Acryloylglycinamide	136–136.5	—	9
Methyl <i>N</i> -Acryloylglycinate	49–52	58–60/3	10
Ethyl <i>N</i> -Acryloylglycinate	35–41	130–135/0.4	11

<sup>a</sup> Unless otherwise stated all the monomers were D, L racemates.

azomethane in tetrahydrofuran and then passed through the columns using a flow rate of 1 ml/min. The angstrom molecular weights thus obtained were multiplied by a standard conversion factor (100 for copolymers containing a preponderance of long-chain alkyl acrylate ester) to obtain weight-average molecular weight.

## MONOMERS

Iso-octyl acrylate was prepared from iso-octyl alcohol<sup>2</sup> and acrylic acid by well-known esterification procedures. The conventional polar comonomers evaluated were all commercial samples used without further purification.

The *N*-acryloylamino acids were prepared according to Kulkarni and Morawetz<sup>3</sup> by reacting an aqueous solution of the sodium salt(s) of the particular amino acid with acryloyl chloride. In most cases, the compounds crystallized in the pure state from the aqueous reaction solution on acidification. Otherwise, a continuous extraction of the aqueous solution with ethyl acetate and a subsequent recrystallization from that solvent afforded the pure compound. The yields in all the reactions were generally good—usually 60–90% of theoretical. The compounds were characterized by examining their nuclear magnetic resonance, infrared, and mass spectra and by comparison, when appropriate, with physical properties reported in the literature. Several new compounds to the general literature were prepared. These were further characterized by elemental analysis or molecular ion exact mass measurement in their mass spectrum. Table I contains a list of the *N*-acryloylamino acids prepared, the melting ranges observed, and references to the literature when appropriate.

Spectral characteristics and analyses of previously unreported compounds that were prepared include the following:

*N*-Acryloyl-*N*-methyglycine:

- IR(KBr): 2700–2400  $\text{cm}^{-1}$  (w) (carboxyl OH)  
1720  $\text{cm}^{-1}$  (s) (C=O)  
1735  $\text{cm}^{-1}$  (s) (C=O)  
1640  $\text{cm}^{-1}$  (s) (C=C)
- NMR(D<sub>2</sub>O): (The pattern was complicated by restricted rotation of the C—N bond).  
3.00, 3.20 $\delta$  (s, 3H, N—CH<sub>3</sub>)  
4.25, 4.35 $\delta$  (s, 2H, —CH<sub>2</sub>CO<sub>2</sub>H)  
5.75–6.90 $\delta$  (m, 3H, CH<sub>2</sub>=CH—)
- Mass spectrum: Molecular ion ( $m/e = 143$ ).  
Analysis: Exact mass for C<sub>6</sub>H<sub>9</sub>NO<sub>3</sub>. Calcd.: 143.058. Found: 143.058

*N*-Acryloyl-*N*-( $\beta$ -cyanoethyl)glycine:

- IR(KBr): 2750–2500  $\text{cm}^{-1}$  (m) (carboxyl OH)  
2205  $\text{cm}^{-1}$  (m) (C $\equiv$ N)  
1740  $\text{cm}^{-1}$  (s) (C=O)  
1730  $\text{cm}^{-1}$  (m) (C=O)  
1640  $\text{cm}^{-1}$  (s) (C=C)
- NMR(D<sub>2</sub>O): (The pattern was complicated by restricted rotation of the C—N bond.)  
2.75–3.00 $\delta$  (m, 2H, —CH<sub>2</sub>CN)  
3.75–4.10 $\delta$  (m, 2H, N—CH<sub>2</sub>—)  
4.30, 4.45 $\delta$  (s, 2H, —CH<sub>2</sub>CO<sub>2</sub>H)  
5.80–7.10 $\delta$  (m, 3H, CH<sub>2</sub>=CH—)
- Mass spectrum: Molecular ion ( $m/e = 182$ ).  
Analysis: Exact mass for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>. Calcd.: 182.069. Found: 182.069.

*N*-Acryloyl-*L*-proline:

- IR(nujol): 2700–2400  $\text{cm}^{-1}$  (w) (carboxyl OH)  
1740  $\text{cm}^{-1}$  (s) (C=O)  
1650  $\text{cm}^{-1}$  (s) (C=C)
- NMR(D<sub>2</sub>O): (The pattern was complicated by restricted rotation of the C—N bond.)  
1.80–2.50 $\delta$  (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)  
3.52, 3.70 $\delta$  [ $t$  ( $J = 6$  Hz), 2H, N—CH<sub>2</sub>—]  
4.40–4.55 $\delta$  (m, 1H, CH—CO<sub>2</sub>H)  
5.70–6.75 $\delta$  (m, 3H, CH<sub>2</sub>=CH—)
- Mass spectrum: Molecular ion ( $m/e = 169$ ).  
Analysis: Exact mass for C<sub>8</sub>H<sub>11</sub>NO<sub>3</sub>. Calcd.: 169.079. Found: 169.074.

*N*-Acryloylnorleucine:

- IR(nujol): 3310  $\text{cm}^{-1}$  (s) (NH)

2700–2400  $\text{cm}^{-1}$  (w) (carboxyl OH)  
 1760  $\text{cm}^{-1}$  (s) (C=O)  
 1720  $\text{cm}^{-1}$  (s) (C=O)  
 1630  $\text{cm}^{-1}$  (s) (C=C)  
 NMR( $\text{D}_2\text{O}$ ): 0.70 $\delta$  [ $t$ ( $J = 5$  Hz), 3H, — $\text{CH}_3$ )  
 1.00–1.50 $\delta$  (m, 4H, — $\text{CH}_2\text{CH}_2\text{CH}_3$ )  
 1.60–2.00 $\delta$  (m, 2H, —CH— $\text{CH}_2$ —)  
 4.30–4.50 $\delta$  (m, 1H, —CH— $\text{CH}_2$ —)  
 5.70–6.50 $\delta$  (m, 3H,  $\text{CH}_2=\text{CH}$ —)  
 Mass spectrum: Molecular ion ( $m/e = 185$ ).  
 Analysis: Exact mass for  $\text{C}_9\text{C}_{15}\text{NO}_3$ . Calcd.: 185.105. Found:  
 185.106

*N*-Acryloylmethionine:

IR(nujol): 3315  $\text{cm}^{-1}$  (s) (NH)  
 2700–2400  $\text{cm}^{-1}$  (w) (carboxyl OH)  
 1735  $\text{cm}^{-1}$  (s) (C=O)  
 1715  $\text{cm}^{-1}$  (s) (C=O)  
 1650  $\text{cm}^{-1}$  (s) (C=C)  
 1225  $\text{cm}^{-1}$  (s) (S— $\text{CH}_2$ —)  
 NMR( $\text{D}_2\text{O}$ ): 2.15 $\delta$  (s, 3H,  $\text{SCH}_3$ )  
 2.00–2.30 $\delta$  (m, 2H,  $\text{CH}_2\text{S}$ )  
 2.55–2.70 $\delta$  (m, 2H, —CH— $\text{CH}_2$ —)  
 4.60–4.70 $\delta$  (m, 1H, —CH— $\text{CH}_2$ —)  
 5.80–6.40 $\delta$  (m, 3H,  $\text{CH}_2=\text{CH}$ —)  
 Mass spectrum: Molecular ion ( $m/e = 203$ ).  
 Analysis: Exact mass for  $\text{C}_8\text{H}_{13}\text{NO}_3\text{S}$ . Calcd.: 203.061. Found:  
 203.060.

*N*-Acryloylaspartic acid:

IR(nujol): 3360  $\text{cm}^{-1}$  (s) (NH)  
 2750–2500  $\text{cm}^{-1}$  (w) (carboxyl OH)  
 1735  $\text{cm}^{-1}$  (s) (C=O)  
 1700  $\text{cm}^{-1}$  (s) (C=O)  
 1655  $\text{cm}^{-1}$  (s) (C=C)  
 NMR( $\text{D}_2\text{O}$ ): 3.00 $\delta$  [ $d$ ( $J = 8$  Hz), 2H, — $\text{CH}_2$ —]  
 4.80 $\delta$  [ $t$ ( $J = 6$  Hz), 1H, —CH—]  
 5.80–6.50 $\delta$  (m, 3H,  $\text{CH}_2=\text{CH}$ —)  
 Mass spectrum: Molecular ion + 1 ( $m/e = 180$ ) (chemical ionization).  
 Analysis: Calcd.: 44.9, 4.8, 7.5. Found: 44.6, 4.8, 7.3  
 (%C,%H,%N):

*N*-Acryloylasparagine:

IR(nujol): 3390  $\text{cm}^{-1}$  (s) (NH)  
 3200  $\text{cm}^{-1}$  (w) (NH)  
 2650–2375  $\text{cm}^{-1}$  (w) (carboxyl OH)  
 1730  $\text{cm}^{-1}$  (w) (C=O)  
 1720  $\text{cm}^{-1}$  (s) (C=O)  
 1660  $\text{cm}^{-1}$  (s) (C=C)

NMR(D <sub>2</sub> O):	2.92 $\delta$ [ $d(J = 8 \text{ Hz})$ , 2H, $-\text{CH}_2\text{CONH}_2$ ] 4.85 $\delta$ [ $t(J = 6 \text{ Hz})$ , 1H, $\text{CHCOOH}$ ] 5.80–6.45 $\delta$ (m, 3H, $\text{CH}_2=\text{CH}-$ )
Mass spectrum:	Molecular ion + 1 ( $m/e = 187$ ) (chemical ionization).
Analysis	Calcd.: 45.2, 5.4, 15.0. Found: 45.1, 5.4, 14.9.
(%C,%H,%N):	

*N*-Acryloyl-5-aminovaleric acid:

IR(KBr):	3275 $\text{cm}^{-1}$ (s) <sub>-1</sub> (NH) · 2775–2550 $\text{cm}^{-1}$ (w) (carboxyl OH) 1695 $\text{cm}^{-1}$ (s) (C=O) 1645 $\text{cm}^{-1}$ (s) (C=C)
NMR(D <sub>2</sub> O):	1.50–1.80 $\delta$ (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ) 2.48 $\delta$ [ $t(J = 6 \text{ Hz})$ , 2H, $-\text{CH}_2\text{C}=\text{O}$ ] 3.30 $\delta$ [ $t(J = 6 \text{ Hz})$ , 2H, $-\text{CH}_2-\text{N}$ ] 5.75–6.35 $\delta$ (m, 3H, $\text{CH}_2=\text{CH}-$ )
Mass spectrum:	Molecular ion ( $m/e = 171$ ).
Analysis:	Exact mass for C <sub>8</sub> H <sub>13</sub> NO <sub>3</sub> . Calcd.: 171.089. Found: 171.092.

## COPOLYMERIZATIONS

In a comparative study such as the present one, it was deemed necessary that an equal number of molecules of the various polar comonomers be compared. Furthermore, the copolymers ideally should have approximately equal molecular weights. Therefore, all of the initial copolymerization reactions were conducted in the following manner: *iso*-octyl acrylate (88.2 g; 0.479 mol), the particular polar comonomer (0.0361 mol), acetone (136 g; 2.35 mol), and azobis(isobutyronitrile) (0.254 g; 0.00155 mol) were charged into a 500-ml amber glass bottle, sparged briefly with nitrogen, and sealed. The solutions thus obtained contained a total monomer mole fraction in the acetone solvent of 0.18 and a molar ratio of 93 parts *iso*-octyl acrylate and 7 parts of the particular comonomer; the initiator concentration was 0.30 mol % based on total moles of monomer. By using such compositions in which the only variable was the particular polar comonomer, it was hoped that the subtle effects imparted by that comonomer could be detected. For example, a monomer containing abstractable hydrogen atoms should curtail the degree of polymerization, resulting in lower copolymer molecular weight. Given constancy of molecular weight in a series of copolymers, on the other hand, the relative strengthening or weakening effect of the comonomer on the internal strength of the copolymer could be determined by appropriate tape tests to be described.

The sealed bottles were shaken at 55°C for 21 hr and then at 60°C for 3 hr. The copolymerization reactions generally produced conversions of about 95% of theoretical, as determined by a standard gravimetric procedure. The copolymer solutions were coated directly onto polyester film for the subsequent tape evaluation.

In the case of the primary amide functional comonomers, *N*-acryloylasparagine and *N*-acryloylglycinamide, solution was not achieved at the 7 molar part level even in the hot acetone-*iso*-octyl acrylate solvent. In those cases the molar concentration was reduced and a small amount of water, i.e., up to 5 wt. % based

on acetone, was added to achieve a homogeneous polymerization solution. The copolymer that formed, however, precipitated from the acetone-water solution. After the usual polymerization period, the polymer mixture was allowed to cool and settle. The supernatant acetone-water was decanted and tetrahydrofuran was added to achieve a clear, colorless, viscous copolymer solution. This solution was then coated and dried for subsequent tape evaluation.

## TAPE TESTS

Historically, pressure-sensitive adhesives have been characterized as possessing a fourfold balance of the properties of adhesion, cohesion, stretchiness, and elasticity.<sup>1,12</sup> For the purpose of this investigation, the "stretchiness and elasticity" descriptions were combined into a "tack" parameter that could be accurately measured. Thus the classical fourfold balance was reduced to a threefold balance of adhesion, cohesion, and tack properties.

For the tape testing procedures the copolymer solutions were knife coated onto polyester film (0.05 mm) to a thickness of about 0.25 mm and dried in an air circulating oven at 88°C for 10 min to remove solvent. The dry coating weight of adhesive was 64.5 g/m<sup>2</sup>. The tape tests were evaluated at 21°C and 50% R.H. and are described below:

**Tape Adhesion Test.** A standard procedure<sup>13</sup> for recording 180° peel adhesion was modified as follows:

1. The polyester film utilized was 0.05 mm in thickness.
2. The peeling rate was about 2 cm/sec.
3. Glass was used as the substrate instead of stainless steel. The adhesion to glass reported was the average of the range of numbers observed for three trials.

**Tape Cohesion Test.** The cohesive strengths of the adhesives were compared by means of a standard shear strength test.<sup>13</sup> Unless otherwise specified, a 500-g load was suspended from an adhesive contact area of 6.4 cm<sup>2</sup> for the measurement. The time required for the tape to separate from the steel plate was measured and recorded in minutes as the average of three trials. In all cases the mode of failure was cohesive in that approximately equal amounts of adhesive remained on both steel and polyester surfaces.

**Tape Tack Test.** The tack measurement was made using a Polyken Probe Tack Tester<sup>14</sup> available from Testing Machines, Inc. The test sample was applied backing side down to a double coated tape (3M Brand No. 665), which in turn was adhered to a small glass coverslide. This apparatus was then adhered test sample adhesive down to one end of a brass cylinder weighing 20 g. The rodlike stainless steel probe (contact area of 0.02 cm<sup>2</sup>) was then brought into contact with the test adhesive in the brass cylinder so that the cylinder was raised and supported by the probe. (The effective pressure forcing the adhesive and the probe into contact was about 1000 g/cm<sup>2</sup>). The cylinder was suspended for 5 sec, and then the probe was withdrawn at a velocity of 1 cm/sec. The maximum force required for removal was measured and recorded. Nine trials were performed for each of the adhesives because of the range of values observed. The highest and lowest values were discarded, and the remaining seven values were averaged.

By the term "balance of properties" in a pressure-sensitive adhesive is meant

that high values are desired for each of the experimentally determined parameters of adhesion, cohesion, and tack. In a comparative study such as this, what is desired is a method to quantitatively assess the effectiveness of the particular polar comonomer for imparting a "balance of properties." The concept of Performance Index (PI) has been adopted to make such comparisons. The PI concept is a very empirical method for effectively subtracting the contribution of the iso-octyl acrylate from the copolymer under investigation; this subtraction procedure also effectively normalizes the PI value. The PI value is computed in the following manner:

$$PI = \left[ \begin{array}{cc} \text{Copolymer} & \text{IOA} \\ \text{Adhesion} & - \text{Homopolymer} \\ & \text{Adhesion} \end{array} \right] + \left[ \begin{array}{cc} \text{Copolymer} & \text{IOA} \\ \text{Tack} & - \text{Homopolymer} \\ & \text{Tack} \end{array} \right] + \left[ \begin{array}{cc} \text{Copolymer} & \text{IOA} \\ \text{Cohesion} & - \text{Homopolymer} \\ & \text{Cohesion} \end{array} \right]$$

It should be noted that the PI value is an index and not a specific value having dimension, since adhesion and tack are recorded in grams and cohesion in minutes.

## RESULTS AND DISCUSSION

Initially, the following comonomers (7 molar parts) were copolymerized with IOA (93 molar parts) using the conditions specified in the Experimental section:

- Acrylic acid (AA)
- Methacrylic acid (MAA)
- Itaconic acid (IA)
- Acrylamide (AM)
- Methacrylamide (MAM)
- Acrylonitrile (AN)
- N*-Vinylpyrrolidone (VP)

In addition, *N*-acryloylglycine (AG) was also evaluated because the monomer contained an interesting "internal blend" of carboxamide and carboxyl functional groups. Molecular weight and viscosity data are given for the series of copolymers in Table II.

The gel permeation chromatography molecular weight value is believed to be precise to  $\pm 10\%$  of the relative value. Thus since 3.0 million was observed with the IOA homopolymer, any deviation from 3.0 million by more than 300,000 can be regarded as significant. Therefore, the MAA and MAM monomers functioned to some extent at least as chain transfer agents. The presence of allylic hydrogen atoms in these monomers could be responsible for this slightly depressed molecular weight. Two of the comonomers, IA and AN, were excluded from addi-

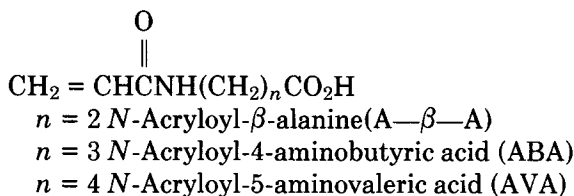
TABLE II  
Polymer Characterization of the IOA Copolymers

Copolymer	Formulation	Viscosity, cps	$M_w, \times 10^6$
1	IOA homopolymer	2600	3.0
2	IOA-AA	3780	3.2
3	IOA-MAA	2320	2.6
4	IOA-IA <sup>a</sup>	448	1.5
5	IOA-AM	4740	3.4
6	IOA-MAM	1620	2.0
7	IOA-AN <sup>a</sup>	1020	1.4
8	IOA-VP	8080	2.7
9	IOA-AG	4680	2.7

<sup>a</sup> These formulations were polymerized an additional 24-hr at 60°C with an additional initiator charge.

tional investigation because the molecular weights and viscosities were quite low, and the formulations polymerized very slowly. The remaining formulations were evaluated as pressure-sensitive adhesives on polyester film. The results of the tape study are given in Table III. The AG-containing adhesive (copolymer 9) performed surprisingly well, producing the highest PI value of the monomers evaluated.

In order to determine what effect proximity of the carboxyl and carboxamide had on adhesive performance when these groups were present in the same molecule as with AG, the following homologs were synthesized and similarly evaluated.



The physical properties and tape data of the homologous series are given in Table IV.

From the above data it was apparent that one methylene unit of separation between carboxyl and carboxamide was preferred as the PI value steadily decreased with increasing separation. Thus the *N*-acryloyl- $\alpha$ -amino acids appeared to offer some promise as components of relatively higher performance acrylic pressure-sensitive adhesives.

In order to investigate the generality of the *N*-acryloyl- $\alpha$ -amino acids as

TABLE III  
Tape Performance of the IOA Copolymers

Copolymer	Formulation	$T_g, ^\circ\text{C}$	Adhesion	Tack	Cohesion	PI
1	IOA homopolymer	-58	1134	107	7	—
2	IOA-AA	-53	1134	163	69	118
3	IOA-MA	-53	1134	168	45	99
5	IOA-AM	-55	1162	152	103	169
6	IOA-MAM	-52	1274	182	93	301
8	IOA-VP	-53	1191	126	25	94
9	IOA-AG	-52	1502	190	141	585



TABLE IV  
Polymer Characterization and Tape Performance of the IOA:*N*-Acryloylamino Acid Copolymers

Copolymer	Formulation	$\bar{M}_w, \times 10^6$	$T_g, ^\circ\text{C}$	Adhesion	Tack	Cohesion	PI
9	IOA-AG	2.7	-52	1502	190	141	585
10	IOA-A- $\beta$ -A	3.2	-52	1361	178	137	429
11	IOA-ABA	3.7	-53	1332	168	134	386
12	IOA-AVA	3.7	-53	1304	172	69	297

components of pressure-sensitive adhesives, the following compounds were synthesized:

- N*-Methacryloylglycine (MG)
- N*-Acryloylalanine (AA1a)
- N*-Acryloylmethylalanine (AMA1a)
- N*-Methacryloylmethylalanine (MMA1a)
- N*-Acryloylnorleucine (ANL)
- N*-Acryloylphenylalanine (APA)
- N*-Acryloylmethionine (AMeth)
- N*-Acryloylaspartic acid (AAS)

These monomers were likewise copolymerized at the 7 molar part level with IOA as before, and their physical properties and tape data are contained in Table V.

The *N*-acryloyl- $\alpha$ -amino acids were clearly superior to the conventional polar comonomers for imparting a balanced set of adhesion, tack, and cohesion properties. The PI values obtained with the *N*-acryloyl- $\alpha$ -amino acids for the 93:7 (mol/mol) formulations in Table V were generally 300 or considerably greater, while the conventional comonomers gave PI values of 300 or considerably less.

Also prepared for evaluation were the primary amide-functional *N*-acryloyl-glycinamide (AGA) and *N*-acryloylasparagine (AAsp). These monomers, however, were not sufficiently soluble in acetone to be evaluated at the 7 molar part level. Their molar concentration was reduced, and results of a tape study are given in Table VI.

A reasonable proposal to explain the superiority of the *N*-acryloylamino acids is that the monomers are at least di- and, in some instances, trifunctional. Thus an IOA-AG (93:7 mol/mol) copolymer, for example, which contains 7 molar parts of  $-\text{CO}_2\text{H}$  and 7 molar parts  $-\text{CONH}-$  should possibly be compared with an

TABLE V  
Polymer Characterization and Tape Performance of the IOA:*N*-Acryloyl- $\alpha$ -amino Acid Copolymers

Copolymer	Comonomer	$M_w, \times 10^6$	$T_g, ^\circ\text{C}$	Adhesion	Tack	Cohesion	PI
13	MG	2.3	-53	1474	204	138	568
14	AA1a	2.7	-52	1474	183	68	477
15	AMA1a	3.1	-52	1247	155	133	287
16	MMA1a	2.1	-48	1588	193	62	595
17	ANL	2.4	-51	1389	202	47	390
18	APA	2.5	-51	1588	167	73	580
19	AMeth	6.7	-54	1588	175	62	577
20	AAS	3.1	-50	1559	268	1050	1629

TABLE VI  
Polymer Characterization and Tape Performance of the IOA:Primary Amide-Functional *N*-acryloyl- $\alpha$ -amino Acid Copolymers

Copolymer	Formulation	$M_w, \times 10^6$	$T_g, ^\circ\text{C}$	Adhesion	Tack	Cohesion
21	IOA-AAsp (99:1 mol/mol)	4.0	-55	1106	111	21
22	IOA-AGA (96.5:3.5 (mol/mol)	6.2	-54	1106	151	274

IOA-AA (86:14 mol/mol) formulation because AA is monofunctional. In order to examine this proposal and to learn whether the  $-\text{CO}_2\text{H}$  group and/or the  $-\text{CONH}-$  group in the *N*-acryloylamino acids was responsible for the unexpectedly higher performance observed, derivatives were prepared in which these hydrogen-bonding, cohesion-building groups were not present. Two ester derivatives, methyl *N*-acryloylglycinate (MAG) and ethyl *N*-acryloylglycinate (EAG), in which only the  $-\text{CONH}-$  group was present and two tertiary amide derivatives, *N*-acryloyl-*N*-methylglycine (AMG) and *N*-acryloyl-*L*-proline (AP), in which only the  $-\text{CO}_2\text{H}$  group was present, were synthesized and copolymerized with IOA. In addition, *N*-acryloyl-*N*-( $\beta$ -cyanoethyl)glycine (A $\beta$ CEG) was also prepared and evaluated to examine the effect of the nitrile function. The results are given in Table VII.

From the relative inability of MAG and EAG above to impart any cohesive strength to the copolymer, it was apparent that the  $-\text{CONH}-$  group in the *N*-acryloylamino acids played a small role in producing the higher adhesive performance. The  $-\text{CO}_2\text{H}$  group evidently was almost completely responsible for the ultimately higher performance observed with the *N*-acryloylamino acid-containing copolymers, and in a comparative study such as this, the *N*-acryloylamino acids could be regarded as effectively monofunctional and compared on an equimolar basis with the conventional comonomers.

The A $\beta$ CEG-containing formulation displayed excellent properties, indicating that the nitrile group indeed had beneficial effects on adhesive performance. Although a similar decrease in molecular weight was observed with A $\beta$ CEG as with AN (copolymer 7), the nitrile function was able to be incorporated into a copolymer very efficiently with the former, whereas AN copolymerized very sluggishly under the solution polymerization conditions described in the Experimental section.

A further consideration concerning the suitability of a particular polar acrylic comonomer for use in a pressure-sensitive adhesive is what effect increasing the concentration of that comonomer in the formulations has on tape performance.

TABLE VII  
Polymer Characterization and Tape Performance of the IOA:Alkylated *N*-Acryloyl- $\alpha$ -amino Acid Copolymers

Copolymer	Formulation (93:7 mol/mol)	$M_w, \times 10^6$	$T_g, ^\circ\text{C}$	Adhesion	Tack	Cohesion	PI
23	IOA-MAG	2.3	-53	1304	129	14	199
24	IOA-EAG	2.2	-56	Adhesive split	128	9	—
25	IOA-AMG	5.0	-50	1729	206	95	782
26	IOA-AP	4.5	-51	1531	209	113	603
27	IOA-A $\beta$ CEG	1.4	-52	1928	245	75	1000

For many pressure-sensitive adhesive uses, a formulation with a substantially higher cohesive strength is required. This increased cohesion is usually achieved by increasing the concentration of the polar comonomer in the copolymer.<sup>15</sup>

Because the copolymers containing AG (copolymer 9) and AAS (copolymer 20) produced excellent tapes with high PI values and because these monomers were quite soluble in the acetone polymerization solvent and could therefore be incorporated at high molar levels, these two monomers were compared in a molar concentration study with AA and AM. [MAM, which was an excellent comonomer with IOA at the 7 molar part level (copolymer 6), produced an insoluble formulation when evaluated in an 86:14 (mol/mol) formulation with IOA and was therefore unsuitable for the study.] The level of the particular comonomer was increased relative to the IOA until the peel adhesion of the resulting tape became "shocky" on removal. "Shockiness" is very undesirable in pressure-sensitive adhesives and is characterized by a very jerky peelback during peel testing such that the peel force will at times register an instantaneous zero value. The physical properties and tape data of the various formulations are given in Table VIII. (Note: The load was increased to 1000 g in the cohesion test, and the adhesive area was reduced to one-quarter of the area used previously in order to produce failures within reasonably short times for the relatively higher performance adhesives containing the higher polar comonomer concentrations.)

Relevant plots of the data contained in Table VIII are given in Figures 1–3. Figure 1 is a plot of adhesion versus increasing molar carboxyl or carboxamide concentration; the dotted lines represent projected maxima. Figure 2 shows the corresponding tack versus functional group level relationships, and Figure 3 shows a plot of cohesion versus functional group concentration.

Examination of the data tabulated in Table VIII and presented graphically in the figures revealed that the *N*-acryloylamino acids exhibited essentially the positive features of both AA and AM. Like AA, the tack values with AG and AAS were quite high, and in addition, high values were observed at lower molar concentration than with AA. The cohesion behavior of the monomers paralleled

TABLE VIII  
The Effect of Increasing Polar Comonomer Concentration on Tape Performance

Copolymer	Comonomer	Mole ratio	$M_w, \times 10^6$	$T_g, ^\circ\text{C}$	Adhesion	Tack	Cohesion
28	AA	86:14	2.5	-47	1247	261	2
29	AA	82.5:17.5	2.5	-45	1378	261	10
30	AA	79:21	2.2	-39	1304	346	16
31	AA	75.5:24.5	2.7	-39	"Shocky"	210	90
32	AM	86:14	2.5	-48	1219	264	106
33	AM	82.5:17.5	2.4	-52	859	255	1421
34	AM	79:21	2.0	-48	"Shocky"	242	10,000+
9	AG	93:7	2.7	-52	1502	190	2
35	AG	89.5:10.5	1.8	-48	1616	321	12
36	AG	86:14	1.8	-46	1616	347	124
37	AG	82.5:17.5	2.9	-44	1276	357	3463
38	AG	79:21	1.7	-46	"Shocky"	279	10,000+
39	AAS	95:5	1.8	-53	2041	192	1
20	AAS	93:7	3.1	-50	1559	268	51
40	AAS	91:9	3.4	-52	1446	349	393
41 <sup>a</sup>	AAS	88:12	3.6	-50	1219	335	2480

<sup>a</sup> The copolymer solution was homogeneous but quite turbid.

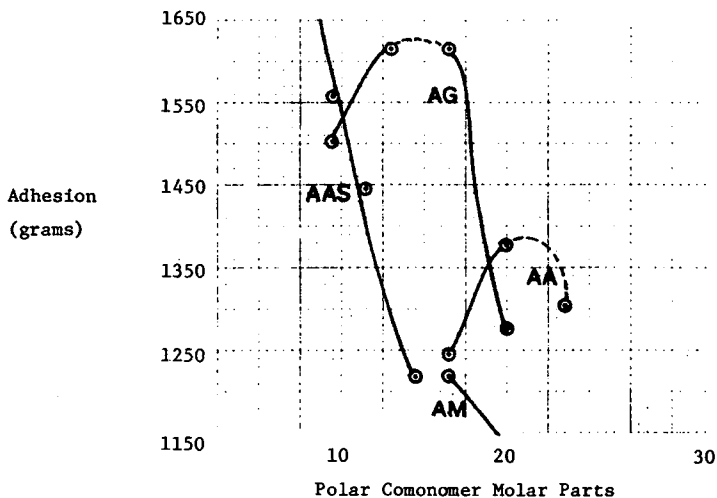


Fig. 1. Plot of adhesion versus increasing molar carboxyl or carboramide concentration.

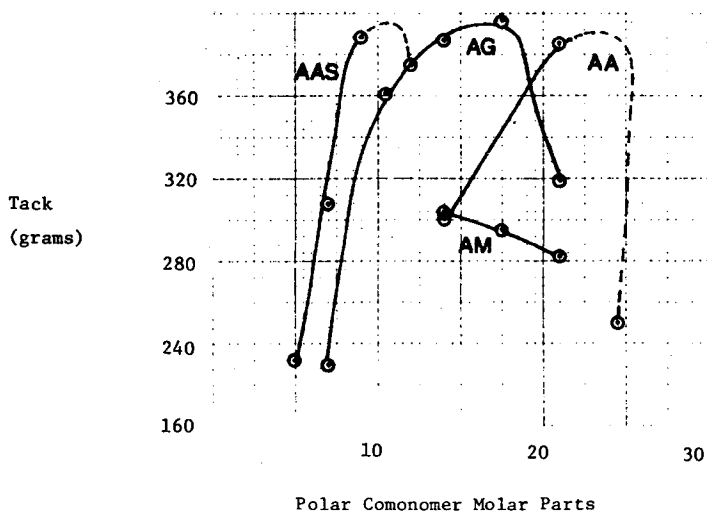


Fig. 2. Plot of tack versus functional group level.

AM very well in that tremendous cohesion was produced at modest molar concentrations. The AG and AAS monomers, on the other hand, exhibited a distinctly higher peel adhesion than with either AA or AM and again also at lower molar concentrations.

## CONCLUSIONS

Several observations can be made concerning the data presented:

1. As expected, comonomers that contained allylic hydrogen atoms produced generally lower molecular weight copolymers. Thus the acrylate-functional monomers were preferred over methacrylates. In addition, the allylic hydrogens may have been responsible for a much slower polymerization rate in the case of itaconic acid (copolymer 4). By the same measure, the nitrile functional group,

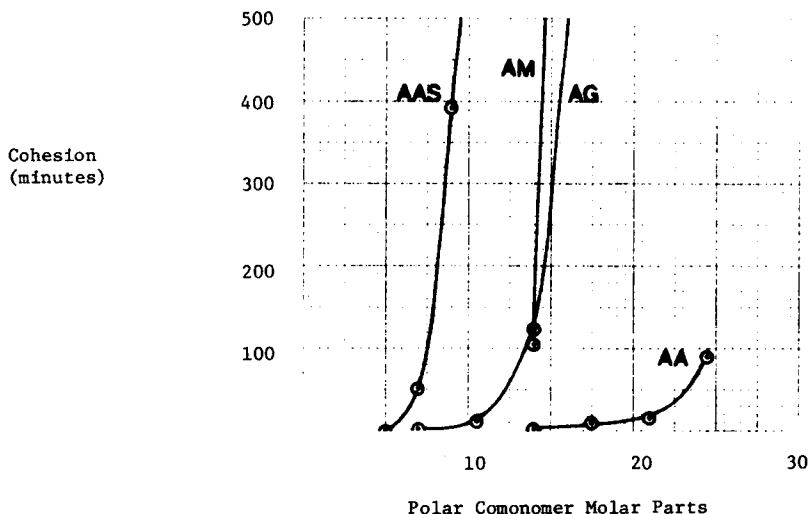


Fig. 3. Plot of cohesion versus functional group concentration.

perhaps via the  $\alpha$ -methylene groups, caused conversion and molecular weight problems with acrylonitrile (copolymer 7). The conversion problem with the nitrile group, however, could be circumvented by using a readily polymerizable acrylamido-functional nitrile as in the case of *N*-acryloyl-*N*-( $\beta$ -cyanoethyl)-glycine (copolymer 27). By use of this latter monomer, it was possible to discern the high adhesion and tack qualities imparted by the nitrile function.

2. For imparting internal strength, monomers with carboxyl and, especially, primary carboxamide groups were preferred. *A priori*, these two functional groups should provide high internal strength, since they are both capable of strong hydrogen-bonding interactions; the superiority of the primary amide to the carboxyl for intermolecular association could also be predicted from the fact that acetic acid is a liquid, while acetamide is a fairly high melting solid even though their molecular weights are almost equal.

3. From a pressure-sensitive adhesive standpoint, the carboxyl group was superior for imparting tack and adhesion but lacked the cohesion-building ability of a primary amide group. The carboxyl was generally preferred over the primary amide, however, because the latter functional monomers were generally insoluble in the polymerization solvents and caused insolubility of the copolymers even at modest concentrations.

4. The *N*-acryloylamino acids provided the high tack of acrylic acid-containing adhesives, the high cohesive strength of acrylamide-containing adhesives, and improved adhesion properties not observed with either acrylic acid or acrylamide. In addition, these improved overall properties were observed at lower molar concentrations with the *N*-acryloylamino acids.

The reason the *N*-acryloylamino acids functioned as well as they did is not presently understood. In connection with the concentration study (copolymers 28-41), it was concluded that the monomers could be regarded as being effectively monofunctional. This was based primarily on the relative failure of the monomers to impart cohesive strength when hydrogen bonding via the carboxyl function was eliminated by esterification (copolymers 23 and 24). This con-

clusion, although accurate for the comparative study, may not be totally suitable for determining just how these monomers function from a structure viewpoint. For one thing, they build cohesion like an acrylamide—indicating the importance of the —CONH— group. Also, if the —CONH— group were unimportant, the study investigating the proximity of the —CONH— and —COOH groups (copolymers 9–12) should have presumably yielded almost equivalent tapes—this was not the case. From a polymer rheology standpoint, examination of the trends in glass transition temperatures in the concentration study (copolymers 28–41) reveals that the transition of the *N*-acryloylamino acids seemed to level off at a much lower temperature than an equimolar acrylic acid-containing formulation. This may indicate that a significant amount of the *N*-acryloylamino acid charge was entering the copolymer as blocks. Just how these “blocks” influence tape properties is a matter of speculation at this time.

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