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The Fundamental Basis for Cyclopolymerization. III. A Spectroscopic Study of Dimethacrylamides*

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SUMMARY

The purpose of this investigation was to prepare suitable solid 1,6-dienes and the corresponding monoenes and to compare their UV and NMR spectra. A comparison of their polymerization characteristics will be reported in the succeeding paper of this series. The compounds chosen for this study were dimethacrylamide, N-isobutyrylmethacrylamide, and their N-methyl and N-phenyl derivatives. Since the dimethacryl derivatives are solids at room temperature, they are suitable monomers for solid-state polymerization studies, the results of which could lead to significant conclusions regarding the fundamental basis for cyclopolymerization. A previously postulated electronic interaction between the neighboring double bonds of the dienes should be detectable when their UV spectra are compared with their monoene counterparts. The UV spectra of the N-isobutyrylmethacrylamides and dimethacrylamides were compared with the spectra of the related diisobutyramides, methacrylamides, and isobutyramides. The spectra of the diacylamides were much more complicated than predicted, and it seems that interaction of the carbonyls through the nitrogen is the major factor affecting the observed spectral transitions. This is different from the corresponding anhydrides in which the carbonyl groups appear to behave as isolated chromophores. The NMR spectra of the compounds were determined since a comparison of chemical shifts and variations of chemical

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*Presented in part at the IUPAC Symposium on Macromolecular Chemistry, Budapest, Hungary, August, 1969 shifts with solvent could be related to the conformational differences of the diacylamides. The chemical shifts, for the most part, were small but were useful in interpreting degree of purity of the monomers, and in drawing certain conclusions concerning the conformations of the compounds. The significance of these conclusions to a suitable explanation for cyclopolymerization will be discussed.

INTRODUCTION

In the previous paper of this series [1] the IR spectral properties of certain 1,6-dienes and the relationship of these properties to the polymerizability of the dienes was discussed. This paper deals with the UV and NMR spectra of certain selected 1,6-dienes and a comparison of these spectra with those of suitable monoene counterparts in each case. The compounds prepared and studied were dimethacrylamide, N-isobutyrylmethacrylamide, and their N-methyl and N-phenyl derivatives. The dimethacrylamides are solids at room temperature which makes them suitable monomers for a solid-state polymerization study.

In an earlier paper [2] it was shown that progressive bathochromic wavelength shifts occurred in the far UV spectra of a series of allyl substituted silanes containing one, two, three, and four allyl substituents. These wavelength shifts are consistent with and are attributed to a homoconjugative, interspacial interaction between the intramolecular double bonds in accord with an earlier suggestion [3] that such an interaction could account for the unique tendency of unconjugated dienes to undergo cyclopolymerization. This type of interaction would exert a stabilizing influence on the excited state of the molecule, thus providing an energetically favorable path from diene to cyclic polymer.

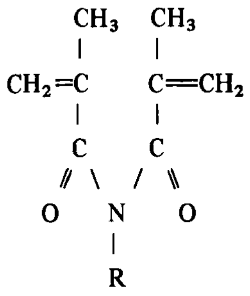
If indeed such an interaction does exist, it should persist in the solid state, and should have an influence on the conformation of the molecule and the relative positions of the intramolecular double bonds in the crystal. If the molecule has a conformation in the crystal favorable for cyclopolymerization to occur in the solid state, a high degree of cyclization would be predicted. On the other hand, a high degree of cyclization resulting from solid-state polymerization of suitable monomers could be interpreted to mean that the molecule does have a favorable conformation for cyclization in the crystal, and that this conformation, otherwise highly improbable, could be accounted for on the basis of the above postulated homoconjugative interspacial interaction between the intramolecular double bonds.

This investigation was undertaken to test these hypotheses. This paper reports an extensive UV and NMR spectral examinatiion of a series of suitable dienes. The polymerization results will be reported in the succeeding paper of this series.

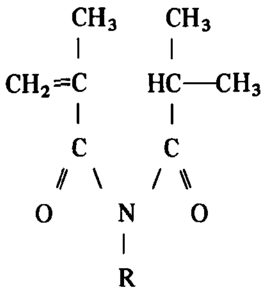
RESULTS AND DISCUSSION

Synthesis of Monomers

The compounds synthesized for this study were the dimethacrylamides (I), the corresponding N-isobutyrylmethacrylamides (II), and also the diisobutyramides (III). Structures of these compounds are shown.



I



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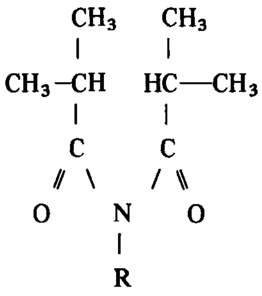


III

R = H, CH_3, or C_6H_5

Sokolova and Rudkovskaya [4] have previously reported the preparation of N-methyldimethacrylamide by heating N-methylmethacrylamide with methacrylic anhydride. Their procedure was used to prepare this diamide. Shortly after this work was started, Götzen and Schröder [5] reported the preparation of dimethacrylamide by heating methacrylamide with methacrylic anhydride. This method was used for the preparation of this compound but the yield was much lower than reported. Götzen and Schröder obtained yields of 29%, while in this work yields varying from 0 to 13% were obtained. Two side reactions contributed to the low yields, polymerization, and dehydration of methacrylamide to methacrylonitrile. In some reactions the yield of methacrylonitrile was 50-60% based upon the amount of methacrylamide used. It has been reported that acid chlorides catalyze the acylation of amides by anhydrides [6] but can in some cases lead to dehydration [7]. When methacrylamide, methacrylic anhydride, and a trace of methacryloyl chloride were heated together, no dimethacrylamide was isolated and a 65% yield of methacrylonitrile was obtained. A yield of greater than 5% dimethacrylamide could be obtained only when the methacrylic anhydride used was prepared from methacryloyl chloride that had been made by the reaction of methacrylic acid, benzenesulfonyl chloride, and pyridine. When commercially available methacryloyl chloride was used, the anhydride obtained must have been contaminated by acidic impurities which caused dehydration rather than acylation.

Attempts were made to prepare N-phenyldimethacrylamide by heating methacrylanilide with methacrylic anhydride. Considerable polymerization occurred and only small amounts of the product were isolated. However, N-phenyldimethacrylamide was readily prepared by the reaction of the sodium salt of methacrylanilide with methacryloyl chloride. Methacrylanilide was added to sodium hydride in tetrahydrofuran (THF) and this solution then added to methacryloyl chloride. If the methacryloyl chloride was added to the sodium salt of methacrylanilide, considerable polymerization occurred, yields were lower, and the product was more difficult to isolate.

An attempt was made to prepare N-phenyldiacrylamide by reacting the sodium salt of acrylanilide with acryloyl chloride by using a procedure identical to that used for the preparation of N-phenyldimethacrylamide. Only polymeric products were obtained and no attempt was made to identify the polymer.

The diisobutyramides were prepared by hydrogenation of the corresponding dimethacrylamides. With all three compounds reduction was shown to be complete by comparison of the NMR spectrum of the starting material with the product.

The mixed diacylamide, N-isobutyrylmethacrylamide, was prepared by heating isobutyric anhydride with methacrylamide. Some dehydration occurred, but little polymer formed so the product was easily isolated. The product was a mixture of the desired N-isobutyrylmethacrylamide and a small amount of diisobutyramide. This was shown by comparing the NMR spectrum of the product with that of diisobutyramide. A multiplet in the spectrum of the product at 6.92 τ corresponds to the methine septet of diisobutyramide. Also the integrated ratio of the methyl protons of the methacryl group to the methyl protons of the isobutyryl group was 1:2.2 rather than 1:2. The pure product could be isolated by a combination of crystallization from water and extraction with chloroform.

Attempts to prepare N-methyl-N-isobutyrylmethacrylamide by heating isobutyric anhydride with N-methylmethacrylamide gave a mixture of products. The reaction of the sodium salt of N-methylmethacrylamide with isobutyryl chloride also gave a mixture of products. Pure N-methyl-N-isobutyrylmethacrylamide was prepared by reacting the magnesium salt of N-methylmethacrylamide with isobutyryl chloride. N-Methylmethacrylamide was added to a solution of ethyl magnesium bromide in THF and this solution was then added to isobutryl chloride. The NMR spectrum was consistent with structure and purity of the product.

N-Phenyl-N-isobutyrylmethacrylamide was prepared by the reaction of the sodium salt of methacrylamide with isobutyryl chloride. The procedure was the same as that used for the preparation of N-phenyldimethacrylamide.

Shortly after the completion of the synthetic work discussed above, Sokolova and Rudkovskaya [8] reported the preparation of dimethacrylamide and its N-methyl, N-propyl, and N-phenyl derivatives. In their procedure the appropriate monomethacrylamide was added to ethyl magnesium bromide in THF. After completion of the reaction the mixture was treated with methacryloyl chloride. The method used by Sokolova and Rudkovskaya, similar to the preparation of N-methyl-N-isobutyrylmethacrylamide described above, would seem to be a better method of preparing the compounds used in this work.

Nuclear Magnetic Resonance Spectra of the Monomers

The NMR spectra of the compounds prepared in this work were compared for two reasons: first, to establish the structure and purity of the mixed diacylamides; and second, it was thought that the comparison of chemical shifts and variations of chemical shift with the solvent could be related to conformational differences of the diacylamides.

The NMR spectra of the related isobutyramides and methacrylamides have been included to see what effect varying the nitrogen substituent had in the simple amides. In the simple amides the nitrogen substituent would have primarily an electronic effect. In the diacylamides the variation of the nitrogen substituent would change the geometry of the imide group, thus having a steric and electronic effect. The chemical shifts of the isobutyramides are listed in Table 1. The chemical shifts show little change. The chemical shifts of the methacrylamides are shown in Table 2. Here again very little variation is observed. The small changes observed could be related to electron donation by the methyl group and the electron withdrawing effect of the phenyl relative to hydrogen.

The chemical shifts of the diacylamides are listed in Table 3. The variations, for the most part, are small. However, the differences in chemical

Table 1. The Proton Chemical Shifts of Some Isobutyramides

	Chemical shift (τ)		
Compound	$CH_3-\underset{|}{\overset{\overset{CH_3{}^a}{|}}{C}}-$	$H-\underset{|}{\overset{|}{C}}-{}^b$	N–X
1 Isobutyramide	8.83	7.53	–
2 N-Methylisobutyramide	8.84	7.48	7.19[c]
3 Isobutyranilide	8.74	7.47	3.0-2.3

[a] Doublet (J = 6.5 Hz).
[b] Septet (J = 6.5 Hz).
[c] Doublet (J = 4.8 Hz).

Table 2. The Proton Chemical Shifts of Some Methacrylamides

	Chemical shift (τ)			
		$CH_2={}^a$		
Compound	$CH_3-\overset{|}{C}={}^a$	trans[b]	cis[b]	N–X
1 Methacrylamide	8.02	4.57	4.22	–
2 N-Methylmethacrylamide	8.02	4.66	4.28	7.13[c]
3 Methacrylanilide	7.93	4.52	4.17	3.1-2.3

[a] Multiplet.
[b] Refers to relationship to carbonyl.
[c] Doublet (J = 4.5 Hz).

shifts were instrumental in establishing the purity of the mixed diacylamides. For N-isobutyrylmethacrylamide (Compound 2, Table 3), notice the difference between the methine protons of Compounds 1 and 2, also the vinyl protons of Compounds 2 and 3. For N-methyl-N-isobutyrylmethacrylamide (Compound 5, Table 3), there are small differences in the allyl protons of Compounds 5 and 6, the methine protons of Compounds 4 and 5, and the vinyl protons of Compounds 5 and 6. Also, the N-methyl protons of Compounds 4 and 6 are both downfield from the N-methyl protons of Compound

Table 3. The Proton Chemical Shifts of Some Diacylamides

Compound	Chemical shift (τ)					
	CH_3–C(–)–CH_3[a]	CH_3–C(–)=	H–C(–)–[b]	$H_2C=$ trans[c]	$H_2C=$ cis[c]	N–X
1 Diisobutyramide	8.81	–	6.92	–	–	–
2 N-Isobutyrylmethacrylamide	8.80	7.97	6.44	4.35	4.15	–
3 Dimethacrylamide	–	7.97	–	4.40	4.23	–
						X=CH_3
4 N-Methyldiisobutyramide	8.81	–	6.73	–	–	6.73
5 N-Methyl-N-isobutyryl-methacrylamide	8.83	7.95	6.90	4.50	4.57	6.78
6 N-Methyldimethacrylamide	–	8.09		4.64	4.80	6.71
						X=φ
7 N-Phenyldiisobutyramide	8.85	–	6.91	–	–	3.0-2.5
8 N-Phenyl-N-isobutyryl-methacrylamide	8.81	8.02	7.09	4.60	4.45	3.0-2.5
9 N-Phenyldimethacrylamide	–	8.04	–	4.49	4.40	3.0-2.5

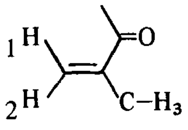
[a] Doublet (J = 6.5 Hz).
[b] Septet (J = 6.5 Hz).
[c] Refers to relationship to carbonyl.

5. For N-phenyl-N-isobutyrylmethacrylamide (Compound 8, Table 3), there are differences in the methine protons of Compounds 7 and 8 and variations in the vinyl protons of Compounds 8 and 9.

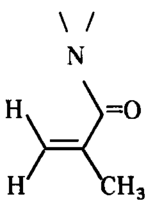
These differences in chemical shifts made it possible to show that the mixed diacylamides did not contain appreciable amounts of the diisobutyramides or dimethacrylamides.

If the chemical shift values of Table 1, 2, and 3 are compared, one can see there is little variation in the $CH_3-\overset{|}{\underset{|}{C}}-CH_3$ protons or in the $CH_3-\overset{|}{C}=$ protons. The largest variation is in the methine protons and, because of the proximity of the carbonyl, this is not surprising. The chemical shifts of the vinyl protons of the diacylamides in Table 3 vary more as the nitrogen substituent changes than do the vinyl protons of the methacrylamides of Table 2. This is probably due to conformational changes in the imide group. Also, the differential chemical shift between the vinyl protons of the methacrylamides is about twice the difference between the vinyl protons of the compounds listed in Table 3.

In Tables 2 and 3 the vinyl protons are assigned as being cis or trans to the carbonyl group. Assignments are based on the work of Jackman and Wiley [9, 10] who showed that for many α, β-unsaturated carbonyl compounds vinyl protons cis to the carbonyl are deshielded to a greater extent than the trans protons. It has also been shown that for many α, β-unsaturated carbonyls (IV), the long-range coupling constant $J_{2,3}$ is larger than $J_{1,3}$ [9, 11]. This was shown to be true for methacrylamide; one exception was methacrylaldehyde [9]. Thus it might be expected that for compounds containing the methacryl group (V), the vinyl proton cis to the carbonyl would be downfield and show less splitting than the upfield proton. This was observed for the vinyl protons of the methacrylamides in Table 2 and for some of the diacylamides (Compounds 2, 3, 8, and 9, Table 3). For N-methyl-N-isobutyrylmethacrylamide (Compound 5, Table 3), and N-methyldimethacrylamide (Compound 6, Table 3), the downfield proton showed the greater splitting. It seemed that for the compounds studied here, the coupling constants would change little so the downfield vinyl proton was assigned as trans to the carbonyl group for Compounds 5 and 6 of Table 3.



IV



V

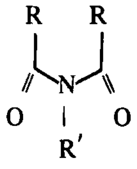
Supporting evidence for the assignment of the vinyl protons of the compounds is found by measuring the solvent shifts (Δ) of the proton resonances produced by benzene. The solvent shift is defined by:

$$\Delta = \tau_{C_6H_6} - \tau_{CDCl_3}$$

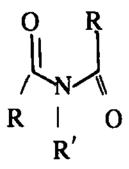
Recently Ronayne and Williams [12] reported that, for a series of α,β-unsaturated acids, the solvent shift ($\Delta = \tau_{C_6H_6} - \tau_{CCl_4}$) is greater for the proton trans to the carbonyl. Similar effects have been reported for vinyl halides, nitriles, and nitro-compounds [12, 13]. For some α,β-unsaturated ketones the solvent shift is greater for the cis proton [10, 14].

The solvent shifts of the compounds prepared in this work which contain the methacryl group (V) are shown in Table 4. For the vinyl protons, the one designated as trans to the carbonyl has the largest shift.

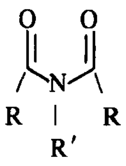
The fact that the vinyl protons of N-methyldimethacrylamide are different from the protons of the N-phenyl and unsubstituted diamides is probably related to conformational differences. The imide group would be expected to exist in three possible conformations—VI, VII, or VIII.



VI



VII



VIII

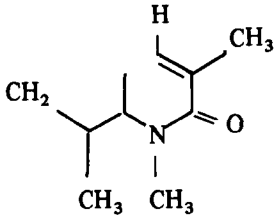
Lee and Kumler [15] have shown that Structure VIII is unlikely because the dipoles are at their closest approach. By comparing the dipole moments

Table 4. Solvent Shifts ($\Delta = \tau_{C_6H_6} - \tau_{CDCl_3}$) of the Proton Resonances of Some Methacrylamides, Dimethacrylamides, and N-Isobutyrylmethacrylamides

	Solvent shifts					
		$H_2C=$				
Compound	$CH_3-\overset{\vert}{C}=$	trans[a]	cis[a]	$CH_3-\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}-$	$H-\underset{\vert}{\overset{\vert}{C}}-$	CH_3-N
1 Methacrylamide	0.26	0.44	0.38	–	–	
2 N-Methylmethacrylamide	0.13	0.25	0.08	–	–	0.25
3 Methacrylanilide	0.07	0.40	0.28	–	–	
4 Dimethacrylamide	0.21	0.45	0.25	–	–	
5 N-Methyldimethacrylamide	0.20	0.52	0.35	–	–	0.17
6 N-Phenyldimethacrylamide	0.17	0.46	0.22	–	–	
7 N-Isobutyrylmethacrylamide	0.30	0.54	0.30	0.05	0.00	
8 N-Methyl-N-isobutyryl-methacrylamide	0.25	0.49	0.35	0.08	0.05	0.32
9 N-Phenyl-N-isobutyryl-methacrylamide	0.17	0.33	0.15	0.09	0.02	

[a] Refers to relationship to carbonyl.

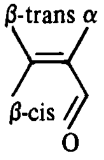
of cyclic, semicyclic, and acyclic imides, they concluded that Conformation VII is favored for acyclic imides. If the imide group is in Conformation VII and the methacryl groups are in an s-trans conformation, so that N-methyldimethacrylamide has a conformation similar to IX, it is possible for the cis-vinyl proton to be located in such a region that it would be shielded by the carbonyl of the other methacryl group.



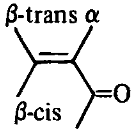
IX

Shielding of the cis-vinyl proton by the carbonyl could shift the cis-vinyl proton upfield of the trans-vinyl proton. In conformation small changes in the geometry of the imide group would change the shielding of the vinyl protons. This could account for the variation of the chemical shifts of the vinyl protons of the diacylamides in Table 3.

Timmons [14] and Fujise and Ito [16] have made a study of the solvent shifts of protons in α,β-unsaturated systems and attempted to relate solvent shifts to the conformation of the system. An α,β-unsaturated carbonyl may exist in two possible coplanar forms—the s-cis (X) and s-trans (XI) [17].



X s-cis



XI s-trans

Timmons studied various α,β-unsaturated ketones. Some had fixed conformations; for others the conformation had been determined by other physical measurements. Fujise and Ito also studied fixed systems and applied the results to labile systems. The shifts expected for a labile s-cis and s-trans systems are:

1. In an s-trans system, α has a smaller Δ than β-trans or β-cis.
2. In an s-cis system, β-cis has a much smaller Δ than β-trans.

If these general tendencies were applied to Table 4, one could conclude that methacrylanilide is in a labile s-trans conformation and N-methylmethacrylamide is in a labile s-cis conformation. The solvent shifts for the protons of methacrylamide do not vary enough to allow assignment of the conformation. Attempts to apply these trends to the diacylamides, Compounds 4-9, were unsuccessful. This is not surprising, considering that these compounds are not simple α,β-unsaturated carbonyl compounds. However, examination of the solvent shifts indicates that Δ values for the same proton in different compounds are similar. It seems that, as far as this method is applicable to these compounds, the conformations are similar.

Ultraviolet Spectra of the Monomers

A study of the UV spectra of the diisobutyramides, N-isobutyrylmethacrylamides, and dimethacrylamides was undertaken to compare the absorptions in the UV spectra of the N-isobutyrylmethacrylamides and dimethacrylamides due to the double bond. Differences in spectra would then be compared with polymerization of the dimethacrylamides. However, the spectra were much more complicated than expected.

Before discussing the results, the typical absorptions expected from a carbonyl, an α,β-unsaturated carbonyl, and an amide will be summarized [18]. A simple energy level diagram for an isolated carbonyl is shown in Fig. 1a. The lowest unoccupied orbital is the antibonding orbital, π^*. The highest occupied orbitals are the lone pair electrons on oxygen in a nonbonding orbital, n, and the bonding π orbital. Two absorptions are commonly observed—at short wavelength a high intensity $\pi \rightarrow \pi^*$ transition and at longer wavelength the low intensity $n \rightarrow \pi^*$ band. Conjugation of the carbonyl with a double bond gives rise to a new system having two occupied bonding π orbitals, π_1 and π_2; two antibonding orbitals, π_3^* and π_4^*; and, finally, the nonbonding pair of electrons on oxygen, n. The two transitions, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, are both shifted to longer wavelengths in an α,β-unsaturated carbonyl.

The energy level diagram for a simple amide, Fig. 2a, contains an additional energy level, P_N, which is the p orbital and electron pair from nitrogen. Three possible transitions for the amide group are shown in Fig. 2a. Two transitions are observed—an $n \rightarrow \pi^*$ band about 210 mμ and a $\pi \rightarrow \pi^*$ transition; the latter can be interpreted as an intramolecular charge

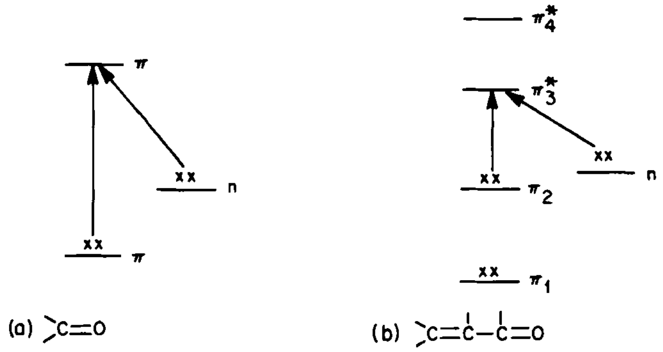


Fig. 1. Energy level diagrams for (a) isolated carbonyl and (b) α,β-unsaturated carbonyl.

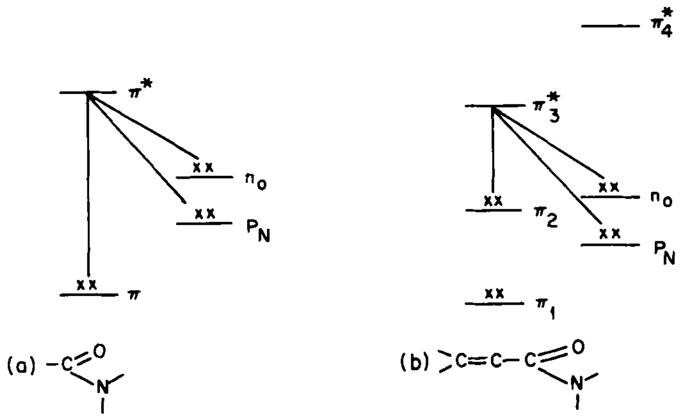


Fig. 2. Energy level diagrams for (a) amide and (b) α,β-unsaturated amide.

transfer from nitrogen to the carbonyl [19, 20]. Theoretical calculations, interpretation of substituent effects, and solvent shifts are consistent with a charge transfer mode [21, 22] for the $\pi \rightarrow \pi^*$ transition.

For the α,β-unsaturated amide, Fig. 2b, once again conjugation leads to two occupied bonding orbitals, two empty antibonding orbitals, the nonbonding electron pair of oxygen, n_O, and p orbital and electron pair of nitrogen, p_N. There are two possible $\pi \rightarrow \pi^*$ transitions. It is possible that with the α,β-unsaturated amide, the π_2 level and the p_N level will have similar energies and both $\pi \rightarrow \pi^*$ transitions will be observed above 180 mμ.

For the isobutyramides in Table 5, increasing solvent polarity caused a red shift in the absorption maximum due to stabilization of the charged excited state. Substitution of methyl for hydrogen also causes a red shift because the inductive effect of the methyl group facilitates removal of an electron from nitrogen. As expected, conjugation of the amide group with a double bond in the methacrylamides causes a bathochromic shift of 15 mμ for the $\pi \rightarrow \pi^*$ bond. The lack of a solvent effect or nitrogen substituent effect upon the absorption maximum could mean the transition is associated with orbitals of the carbonyl system. But with the limited data available, one can not exclude a nitrogen to carbonyl charge transfer band or the possibility of two overlapping bands.

Absorption maxima for some diacylamides are listed in Table 6. All the compounds listed undergo a bathochromic shift as the polarity of the solvent increases. The solvent shifts are small and in the direction that would be expected if the transition involved excitation of the electrons on nitrogen to the carbonyl. The only difference observed is that the methyl diacylamides are the same in acetonitrile and ethanol, while the unsubstituted diacylamides are shifted 2 mμ in going from acetonitrile to ethanol. This must be due to hydrogen bond formation between N—H and the solvent.

The effect of increasing unsaturation in the series diisobutyramide, N-isobutyrylmethacrylamide, and dimethacrylamide is best seen by plotting molar absorptivity vs wavelength. These are shown in Figs. 3 and 4 for the unsubstituted diacylamides and methyl substituted diacylamides, respectively. Diisobutyramide has an intense band with a maximum at 203 mμ; for the methyl derivative this band is at 217 mμ. This band is probably similar to the band in amides; transfer of an electron from nitrogen to carbonyl and substitution of methyl for hydrogen would facilitate removal of an electron from nitrogen.

It might be expected that conjugation of the carbonyls with double bonds, as in dimethacrylamide, would give a spectrum similar to that expected for two α,β-unsaturated carbonyls. This would mean a shift to longer wavelengths of the observed $\pi \rightarrow \pi^*$ band. This apparently is not what happens in the dimethacrylamides. Examination of the spectra of the diacylamides in Fig. 3 and the methyl derivatives in Fig. 4 show that as the isobutyryl group is exchanged for the methacryl group there is a general increase in absorption in the region 175-250 mμ. For the diacylamides in Fig. 3, the band at 210 mμ for N-isobutyrylmethacrylamide and at 214 mμ for dimethacrylamide could be due to a single transition or, considering the broadening of the band, could be two overlapping bands. Also, one can see the beginning absorption of a new band in the region below 190 mμ.

Table 5. Ultraviolet Absorptions of Some Amides

Compound	Heptane λ_{max} (ϵ) (mμ)	Acetonitrile λ_{max} (ϵ) (mμ)	
1 Isobutyramide	178[a]	180 (6,730)	218 (80)
2 N-Methylisobutyramide	182 (6,500)	185 (6,770)	
3 Methacrylamide	Insoluble	199 (11,900)	
4 N-Methylmethacrylamide	199 (10,500)	199 (10,600)	

[a] Solvent, hexane-propionitrile [23].

Table 6. Ultraviolet Absorptions of Some Diacylamides

Compound	Heptane λ_{max}(ϵ) (mμ)	Acetonitrile λ_{max} (ϵ) (mμ)	95% Ethanol λ_{max} (ϵ) (mμ)
1 Diisobutyramide	203 (12,300)	204 (12,000)	206 (11,800)
2 N-Isobutyrylmethacrylamide	210 (13,300)	212 (12,600)	214 (11,900)
3 Dimethacrylamide	214 (14,100)	216 (14,000)	219 (14,000)
4 N-Methyldiisobutyramide	217 (8,600)	220 (8,680)	220 (8,500)
5 N-Methyl-N-isobutyryl-methacrylamide	217 (7,550)	221 (7,770)	221 (8,030)
6 N-Methyldimethacrylamide	217 (10,000)	222 (9,470)	224 (9,800)

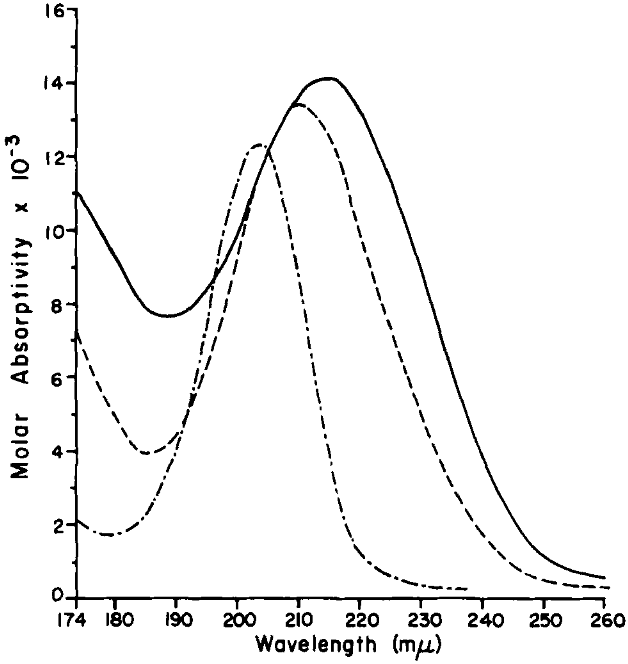


Fig. 3. Ultraviolet spectra of diisobutyramide (- ·), N-isobutyrmethacrylamide (- -), and dimethacrylamide (—) in heptane.

For the N-methyl diacylamides in Fig. 4, the spectra are even more complex. The increased absorption in the region below 210 mμ for N-methyldimethacrylamide is almost certainly due to the appearance of two new absorption bands. The absorptions above 210 mμ could be similar to the band in N-methyldiisobutyramide.

It is apparent that the dimethacrylamides do not behave as two isolated α,β-unsaturated carbonyl systems. The spectra in Figs. 3 and 4 must be composed of two, three, or possibly four overlapping bands. This probably comes about because of the conjugation of the carbonyl groups through the nitrogen. This would lead to possible transition involving the α,β-unsaturated carbonyl system and others associated with the diacylamide group. These transitions must be of similar energy, thus producing overlapping bands.

It is interesting to compare the diacylamides with the related anhydrides listed in Table 7 [24].

The anhydrides in Table 7 behave as though the carbonyls do not

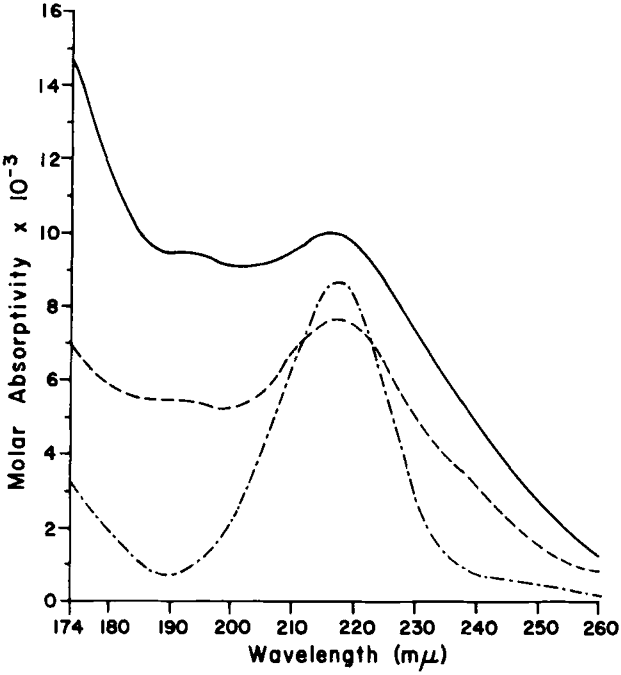


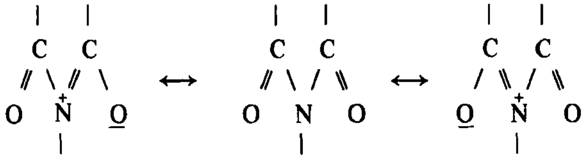
Fig. 4. Ultraviolet spectra of N-methyldiisobutyramide (- ·), N-methyl-N-isobutyrylmethacrylamide (- -), and N-methyldimethacrylamide (—) in heptane.

Table 7. Ultraviolet Absorptions of Methacrylic Anhydride and Related Compounds

Compound	λ_{max} (ϵ) (mμ)	Reference
1 Isobutyric anhydride	230 (124)	This work
2 Methacrylic propionic anhydride	209 (9,700)	24
3 Methacrylic anhydride	209 (19,000)	24
4 Methyl methacrylate	201 (8,600)	24

interact through oxygen. Isobutyric anhydride has a maximum absorption at 230 mμ, extinction coefficient 124. This is what would be expected for two isolated carboxylic acid n → π* bands. Methacrylic anhydride and methacrylic propionic anhydride both have an absorption maximum at 209 mμ. Also, the extinction coefficient for methacrylic anhydride is about twice that of the mixed anhydride.

It seems that in the diacylamide, conjugation through the nitrogen occurs, but conjugation through oxygen in the anhydrides does not. This could be due to the difference in energy of the unshared electrons on oxygen and nitrogen. The electrons on nitrogen are at a higher energy and interact with the carbonyls more strongly than do the electrons on oxygen. In terms of resonance this means XIIa and XIIc contribute more to the structure of the diacylamides than the corresponding resonance forms contribute to the structure of the anhydrides.



XIIa XIIb XIIc

The spectra of the phenyl substituted amides and diacylamides are even more complex than those discussed above. In addition to absorption bands associated with the amide, diacylamide, or α,β-unsaturated group, there are also absorptions associated with the phenyl group. Benzene [25, 18] has three bands in the region above 180 mμ. There are bands at 184 (60,000), 203 (7,500), and 254 (204). The 254 mμ band is referred to as the secondary band, the 203 band as the primary band, and the 184 band the second primary band. In substituted benzenes all of these bands are shifted, usually to longer wavelengths, and the intensity also varies [18]. Substituents with lone pair electrons cause the largest shift and the greater the resonances between the substituent and the ring, the larger the shift.

The spectra of isobutyranilide and methacrylanilide are shown in Fig. 5. In both compounds there are two bands. The long wavelength band is believed to be the shifted primary band of benzene and the short wavelength band the shifted second primary band. The secondary band is apparently submerged by the intense long wavelength band.

One would also expect to find π → π* and n → π* bands associated with

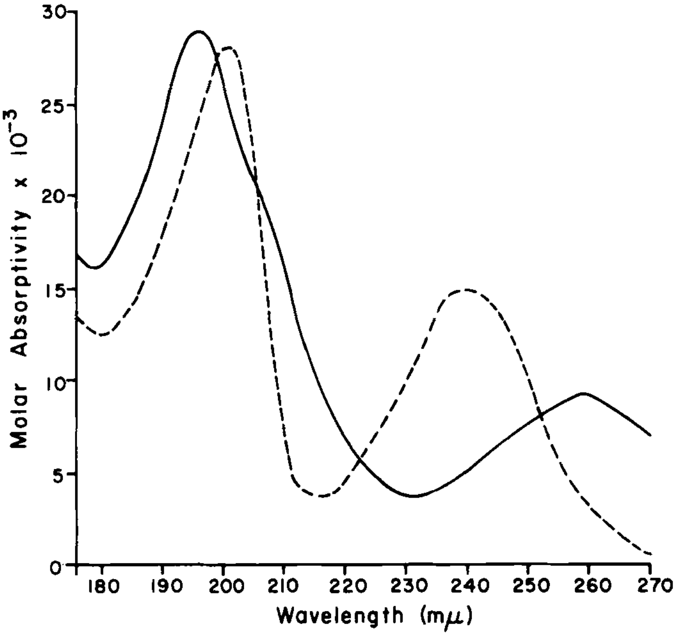


Fig. 5. Ultraviolet spectra of isobutyranilide (- -) and methacrylanilide (–) in heptane.

the amide group. The n → π* would be submerged by the more intense bands of the phenyl group, but it is possible that the band about 195-200 mμ is caused by the overlapping of the π → π* band and the second primary band of the phenyl ring.

The spectra of the phenyl substituted diacylamides are shown in Fig. 6. For these compounds the spectra are composed of broad overlapping bands. All have an absorption maximum in the region 180-190 mμ which could be the second primary band of the ring. There is also a shoulder about 215 mμ which is probably the first primary band. The UV absorptions of the phenyl substituted compounds are listed in Table 8.

Comparison of the two amides with the three diacylamides of Table 8 shows that both bands occur at shorter wavelengths in the diacylamides than in the amides. This could be due to decreased resonance interaction in the diacylamides. Resonance between the diacylamide group and the phenyl group would be expected to be less than that between the amide group and the phenyl group for two reasons. The two carbonyl groups on nitrogen

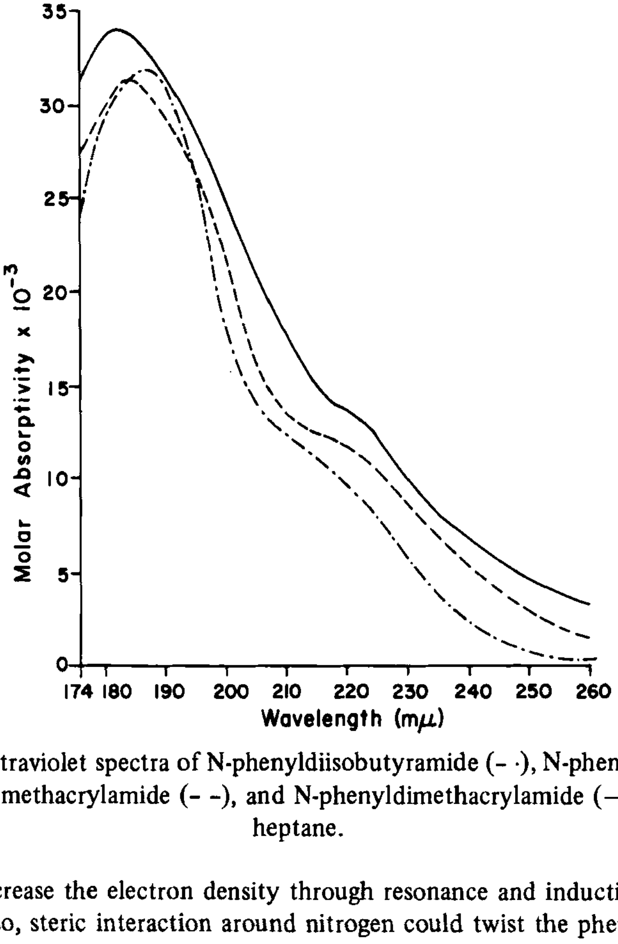


Fig. 6. Ultraviolet spectra of N-phenyldiisobutyramide (- ·), N-phenyl-N-isobutyrylmethacrylamide (- -), and N-phenyldimethacrylamide (–) in heptane.

would decrease the electron density through resonance and inductive effects. Also, steric interaction around nitrogen could twist the phenyl ring so that the p orbital of nitrogen and the conjugated system of the ring are no longer parallel.

The primary band of isobutyranilide is at 240 mμ, while that of methacrylanilide is at 260 mμ. This could be explained in terms of resonance interaction, in which electron donation by the double bond decreases the electronegativity of the carbonyl, thus increasing electron density on nitrogen.

The purpose of studying the UV spectra of the diacylamides was to compare absorptions in the spectra of the N-isobutyrylmethacrylamides and dimethacrylamides associated with the double bond. However, the spectra were more complicated than expected and assignment of the observed

Table 8. Ultraviolet Absorptions of Some Phenyl Substituted Amides and and Diacylamides in Heptane

	Compound	λ_{max} (ϵ) (mμ)	
1	Isobutyranilide	200 (28,200)	240 (15,200)
2	Methacrylanilide	196 (29,200)	260 (8,850)
3	N-Phenyldiisobutyramide	186 (31,600)	213 (11,500)[a]
4	N-Phenyl-N-isobutyryl-methacrylamide	184 (31,400)	218 (11,700)[a]
5	N-Phenyldimethacrylamide	181 (33,800)	218 (13,800)[a]

[a] Shoulder.

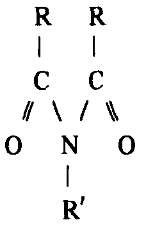
transitions was not possible. For the unsubstituted and N-methyl substituted diacylamides, the observed transitions seemed to be associated with the imide group. In the phenyl substituted diacylamides, the UV spectra were dominated by bands associated with the phenyl group.

CONCLUSIONS

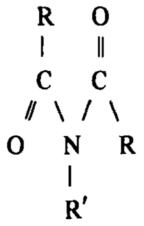
The purpose of this work was to compare the UV spectra and polymerization of the dimethacrylamides with the N-isobutyrylmethacrylamides. In particular, we were interested in the possibility that nonconjugated interactions between the double bonds could be demonstrated by comparing spectral differences between the two types of compounds and these could be related to their ability to cyclopolymerize.

The UV spectra of the compounds have already been discussed. The spectra of the diacylamides were much more complicated than expected and it seemed that interaction of the carbonyls through the nitrogen was the major factor affecting the observed spectral transitions. Because of this interaction, the double bonds in the dimethacrylamides are not truly isolated, and conjugated interactions of the unsaturated carbonyl systems through nitrogen are probably more important than nonconjugated, across space interactions.

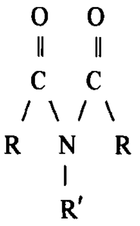
It also appears that the most stable conformations of the diacylamides do not favor interaction between the double bonds. The conformation of the dimethacrylamides will be determined by the conformation of the imide group and that of the methacryl group. The imide group can exist in three coplanar conformations: cis-cis (XIII), cis-trans (XIV), or trans-trans (XV).



XIII cis-cis

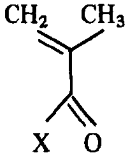


XIV cis-trans

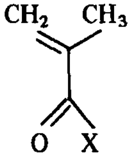


XV trans-trans

In the trans-trans conformation, the carbonyl groups are parallel and this conformation seems unlikely because of electrostatic repulsions. Of the two remaining conformations, measurements of dipole moments [15] indicate diacetamide and N-methyldiacetamide exist in the cis-trans conformation. Because of the size of the methacryl group, it seems that the cis-trans conformation would also be favored for the dimethacrylamides. In addition to the imide group, the conformation of the methacryl group must be considered. The methacryl group exists in two coplanar forms, s-cis (XVI) and s-trans (XVII).



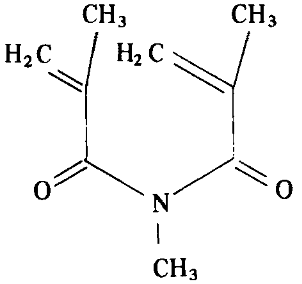
s-trans XVI



s-cis XVII

The s-trans conformation is of lower energy. If X is large and steric repulsions prevent coplanarity of the carbonyl and the double bond, the s-cis conformation is favored. Conformations in which the carbonyl and double bond are not coplanar are unfavorable because of reduced overlap of the π bonds.

Conformations favoring nonconjugated interactions such as XVIII can be achieved only if the carbonyls are brought close together or by twisting the methacryl group out of a coplanar conformation. For this reason, conformations favoring the proposed interaction seem unlikely. The most probable conformation of the diacylamides used in this study is the cis-trans form of the imide group, which allows the methacryl group to be planar.



XVIII

EXPERIMENTAL

UV spectra were obtained with a nitrogen-purged Beckman Model DK-2A Ratio Recording Spectrophotometer equipped with far UV silica optics and cells. Wavelengths were calibrated with mercury emission lines. A nitrogen purge of 1.5 ft^3/min was used below 190 mμ and a purge of 0.3 ft^3/min was used between 190 and 210 mμ. Solution spectra were determined with concentrations between 10^{-3} and 10^{-1} M, using 0.01 cm for UV cells.

NMR spectra were obtained on a Varian A-60A Analytical NMR Spectrometer. The chemical shifts were measured in deuterochloroform, using tetramethylsilane (TMS) as an internal reference. Approximately 1-2% (w/v) solutions were used. The solvent shifts were determined, using approximately 5% solutions in deuterochloroform and benzene, with TMS as an internal reference.

IR spectra were obtained with a Beckman IR-8 Infrared Spectrophotometer or a Beckman IR-10 Infrared Spectrophotometer.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

All common solvents and reagents were reagent grade products. The sources were Fisher Scientific Company, J. T. Baker Chemical Company, Matheson, Coleman and Bell and Eastman Organic Chemicals. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride or dried over molecular sieves before use. Methacryloyl chloride was obtained from Borden Chemical Company and used as obtained, or prepared as described below. Methacrylic acid was obtained from Borden Chemical Company and vacuum distilled before use. Methacrylamide was also obtained from Borden Chemical Company and vacuum sublimed, 90° (0.1 mm) before use, mp 109-110°.

Isobutyric anhydride, isobutyryl chloride, succinic anhydride, gultaric anhydride, and methyl amine hydrochloride were obtained from Eastman Organic Chemicals and used as received. Isobutyramide was obtained from Eastman Organic Chemicals and vacuum sublimed, 100° (0.1 mm) before use, mp 130°. Aqueous methyl amine was obtained from Aldrich Chemical Company and used as received. A 50% dispersion of sodium hydride in mineral oil was obtained from Foote Mineral Company and used as received. Spectrograde solvents were obtained as follows: heptane from Fisher Scientific Company, acetonitrile from Eastman Organic Chemicals, and 95% ethanol from Union Carbide.

Methacryloyl Chloride. This compound was prepared according to the procedure of Heyboer and Staverman [26]. Yield: 84%; bp 97-99°.

Methacrylic Anhydride. This compound was prepared according to the procedure of Yakubovich and co-workers [27]. Yield: 84%; bp 81-83° (10.5 mm); n_D^{25} 1.4550. Literature: [27] bp 63-65° (2.0 mm); n_D^{25} 1.4530.

N-Methylmethacrylamide. This compound was prepared according to the procedure of Heyboer and Staverman [26]. Yield: 76%; bp 84-85° (4 mm); n_D^{25} 1.4742. Literature: [26] bp 88° (5.5 mm); n_D^{20} 1.4740.

N-Methylisobutyramide. This compound was prepared by the method used for the preparation of N-methylmethacrylamide. Yield: 50% bp 111° (18 mm); mp 20°. Literature: [28] bp 110° (17 mm); mp 20°.

Methacrylanilide. A solution of 186 g (2.0 moles) of distilled aniline and 700 ml of benzene was placed in a 2-liter, three-necked flask equipped with a mechanical stirrer, constant-pressure addition funnel, reflux condenser, and drying tube. A mixture of 104 g (1.0 moles) of methacryloyl chloride in 100 ml of benzene was added dropwise and the mixture stirred overnight. After the addition of 500 ml of water, the benzene layer was separated and extracted with two 200-ml portions of 1 N hydrochloric acid and two 200-ml portions of 10% sodium carbonate, then dried over anhydrous sodium sulfate. The benzene was evaporated, using a rotary evaporator, and the crystals remaining were recrystallized twice from hexane-acetone. Yield: 111 g (69%); mp 84-85°. Literature: [29] mp 85°.

Isobutyranilide. This compound was prepared by the procedure used for methacrylanilide. Yield: 84%; mp 105°. Literature: [30] mp 105°.

Dimethacrylamide. This compound was prepared, using the procedure of Götzen and Schröder [5]. Yield: 13%; mp 103-105°. Literature: [5] mp 103-105°.

N-Methyldimethacrylamide. This compound was prepared by using an adaptation of the procedure developed by Sokolova and Rudkovskaya [4]. A mixture of 45 g (0.45 moles) of N-methylmethacrylamide and 75 g (0.48 moles) of methacrylic anhydride, to which small amounts of pyrogallol and copper powder were added to prevent polymerization, was placed in a 200-ml, two-necked flask equipped with a magnetic stirrer, reflux condenser, drying tube, and a thermometer. The contents of the flask were heated for 2 hr at a reaction mass temperature of 145-150°. The contents of the flask were then vacuum distilled bulb to bulb. The fraction distilling below 110° (4.0 mm) was collected and placed in a refrigerator for 48 hr. The crystals that formed were collected by suction filtration, recrystallized twice from heptane, and then vacuum sublimed, 85° (10 mm). Yield: 18.0 g (23%); mp 89.5-90°. Literature: [4] mp 90.5-91.5°.

N-Phenyldimethacrylamide. A 250-ml, three-necked flask was equipped with a mechanical stirrer, pressure-equalizing addition funnel, reflux condenser, and a nitrogen inlet/bubbler. Before assembling, the glassware was baked in an oven overnight at 150°, assembled, and the apparatus flamed out under nitrogen. The flask was charged with 5.0 g of a 50% dispersion of sodium hydride in mineral oil and 35 ml of THF. A solution of 16.1 g (0.10 moles) of methacrylanilide in 30 ml THF was placed in the funnel and added to the sodium hydride over a 3-hr period. Stirring was continued for an additional 1/2 hr.

Into a 250-ml, three-necked flask, assembled and equipped as described above, were placed 12.4 g (0.119 moles) of methacryloyl chloride and 50 ml of THF. The sodium salt of methacrylanilide, prepared as above, was transferred to the addition funnel and added to the acid chloride over a 2-hr period. The mixture was stirred an additional hour, then 10 ml of methanol were added. The reaction mixture was poured into 300 ml of hexane, the solid filtered out, and the solvent evaporated, using a rotatory evaporator. The residue was recrystallized twice from ether. Yield: 11.5 g (50%); mp 79-79.5°. Literature: [8] mp 80-80.5°.

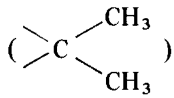
N-Phenyl-N-isobutyrylmethacrylamide. This compound was prepared by a procedure similar to that used for the preparation of N-phenyldimethacrylamide. Yield: 9.6 g (42%); bp 86.5° (0.05 mm), n_D^{25} 1.5205, D_4^{25} 1.0436. The NMR spectrum had absorptions at 2.5-3.0 (C_6H_5), 4.45, 4.60 ($H_2C=$), 7.09 ($H-\overset{|}{C}-$), 8.02 ($CH_3-C=$), and 8.81 τ ($CH_3-\overset{|}{\underset{|}{C}}-CH_3$) with the expected ratio 5:2:1:3:6.

The IR spectrum of the liquid showed the following absorptions: 3180, 3140, 2980, 1695, 1635, 1600, 1498, 1450, 1375, 1355, 1315, 1265, 1175, 1120, 1090, 965, 915, 840, 750, and 690 cm^{-1}. Analysis calculated for $C_{14}H_{17}NO_2$: %C, 72.70; %H, 7.41; %N, 6.05. Found: %C, 72.60; %H, 7.50; %N, 6.20.

N-Methyl-N-isobutyrylmethacrylamide. A 500-ml, three-necked flask equipped with a mechanical stirrer, pressure-equalizing addition funnel, reflux condenser, and nitrogen inlet was flamed and flushed with nitrogen. A static nitrogen atmosphere was maintained throughout the reaction. The flask was charged with 4.4 g (0.18 moles) of magnesium turnings and 50 ml of THF (dried over molecular sieve). A few drops of ethyl bromide were added and stirred until reaction started, then 16.4 g (0.15 moles) of ethyl bromide in 50 ml of THF were added at such a rate as to maintain a gentle reflux, and stirring was continued an additional 2 hr.

A solution of 14.7 g (0.15 moles) of N-methylmethacrylamide in 50 ml of THF was placed in the addition funnel and added to the Grignard reagent over a 2-hr period, after which 300 ml of THF were added to keep the magnesium salt of the amide in solution.

A 1-liter, three-necked flask was equipped as described above. The flask was charged with 15.9 g (0.15 moles) of isobutyryl chloride and 50 ml of THF. The magnesium salt of N-methylmethacrylamide, prepared as above, was transferred to the addition funnel and added dropwise with stirring to the isobutyryl chloride over a 10-hr period.

After stirring an additional hour, 10 ml of methanol were added and the THF evaporated, using a rotatory evaporator. The residue was triturated with 200 ml of water and the aqueous solution extracted with 200 ml of ether. The ether solution was separated and dried over anhydrous sodium sulfate. After distilling off the ether, the product was fractionated through a 28-plate spinning band column. Yield: 8.0 g (32%); bp 101° (15.5 mm); n_D^{25} 1.4592, D_4^{25} 0.993. NMR supported the structure with absorptions centering at 4.50, 4.57 (=CH_2), 6.78 (N–CH_3), 6.90 ($-\overset{|}{\underset{|}{C}}-H$), 7.95 ($=\overset{|}{C}-CH_3$), and 8.83 τ () in the expected areas of 2:4:3:6.

The IR spectrum of the liquid showed the following absorptions: 2980, 2945, 2890, 1690, 1660, 1635, 1450, 1380, 1325, 1260, 1220, 1065, and 920 cm^{-1}. Analysis calculated for $C_9H_{15}NO_2$: %C, 63.87; %H, 8.95; %N, 8.28. Found: %C, 63.58; %H, 8.93; %N, 8.08.

N-Isobutyrylmethacrylamide. This compound was prepared by heating isobutyric anhydride and methacrylamide. Into a 500-ml, three-necked flask, equipped with a distilling head, drying tube, thermometer, and magnetic stirrer were placed 120 g (0.76 moles) of isobutyric anhydride, 42.5 g (0.50 moles) of methacrylamide, and a trace of iodine as an inhibitor. An oil bath was used to heat the flask to a reaction mass temperature of 150°, and the oil bath was then maintained at a temperature of 150° for 2 hr.

After cooling, the magnetic stirring bar was removed and the drying tube replaced by a nitrogen capillary bubbler reaching to the bottom of the flask. The reaction mixture was vacuum distilled at 6.0 mm until the contents of the flask began to solidify. The solid mass was dissolved in ether, filtered, the ether evaporated, and the crystals washed with hexane, and finally vacuum sublimed. Yield: 28 g; mp 124-126°. The presence of absorptions in the NMR spectrum at 6.92 and 6.44 τ and a $=\overset{|}{C}-CH_3$ to $CH_3-\overset{|}{\underset{|}{C}}-CH_3$ proton ratio of 1:2.2 indicated the product was a mixture of N-isobutyrylmethacrylamide and a small amount of diisobutyramide.

A pure sample of mixed diamide was obtained by dissolving 10 g of the mixture in 400 ml of boiling water, cooling to room temperature, and filtering off the crystals which formed. The filtrate was extracted with 100 ml of chloroform. After drying over anhydrous sodium sulfate, the chloroform was evaporated and the crystals remaining were vacuum sublimed at 95° (0.1 mm). Yield: 4.2 g; mp 123.5-124.5°. The NMR spectrum is consistent with the proposed structure, showing the following absorptions: 4.10 and 4.37 (=CH_2), 6.46 ($-\overset{|}{\underset{|}{C}}-H$), 7.99 ($=\overset{|}{C}-CH_3$), and 8.80 τ ($CH_3-\overset{|}{\underset{|}{C}}-CH_3$), with the expected ratio 2:1:3:6.

The IR spectrum (KBr pellet) showed the following absorptions: 3280, 3190, 2920, 1725, 1690, 1635, 1500, 1390, 1315, 1160, 938, and 800 cm^{-1}. Analysis calculated for $C_8H_{13}NO_2$: %C, 61.92; %H, 8.44; %N, 9.02. Found: %C, 61.77; %H, 8.51; %N, 8.85.

Diisobutyramide. A sample of this compound was prepared by the hydrogenation of dimethacrylamide. A pressure bottle was charged with 2.0 g of dimethacrylamide, 30 ml of ethanol, and a small amount of a 5% palladium on charcoal catalyst. Hydrogenation was carried out using a Parr hydrogenation apparatus. The initial hydrogen pressure was at 25 lb. After shaking 6 hr, the bottle was opened, the catalyst filtered out, ethanol evaporated, and the crystals vacuum sublimed. Yield: 1.8 g; mp 175°. Literature: [31] mp 175°.

N-Methyldiisobutyramide. This compound was prepared by the hydrogenation of N-methyldimethacrylamide by a procedure similar to that used for diisobutyramide. Yield: 4.5 g; bp 86° (5.5 mm); n_D^{25} 1.4460; D_4^{25} 0.962. The NMR spectrum is consistent with the proposed structure—a singlet at 6.33 τ ($N-CH_3$), a septet centered at 6.73 τ ($-\overset{|}{\underset{|}{C}}-H$), and a doublet at 8.81 τ ($CH_3-\overset{|}{\underset{|}{C}}-CH_3$). The ratio of the sum of the $N-CH_3$ and $-\overset{|}{\underset{|}{C}}-H$ protons to the $CH_3-\overset{|}{\underset{|}{C}}-CH_3$ protons is 4.9:12 (theoretical 5:12). Analysis calculated for $C_{19}H_{17}NO_2$: %C, 63.12; %H, 10.01; %N, 8.18. Found: %C, 62.98; %H, 10.02; %N, 8.40.

N-Phenyldiisobutyramide. This compound was prepared by the hydrogenation of N-phenyldimethacrylamide. Yield: 4.5 g; bp 90° (0.35 mm). Upon standing, the product crystalized, mp 35.5-36.5°. The NMR spectrum is consistent with the proposed structure—a multiplet at 2.5-3.0 τ (C_6H_5), septet at 6.91 τ ($-\overset{|}{\underset{|}{C}}-H$), and a doublet at 8.81 τ ($CH_3-\overset{|}{\underset{|}{C}}-CH_3$). The ratio of the proton areas is 5:2:12 (theoretical 5:2:12). Analysis calculated for $C_{14}H_{19}NO_2$: %C, 72.08; %H, 8.21; %N, 6.00. Found: %C, 71.96; %H, 8.39; %N, 5.98.

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