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Copolymerization of *N*-vinyl phthalamide with acrylate and methacrylate monomers and preliminary analysis of the stereochemistry of poly(*N*-vinyl phthalamide)

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Summary

N-Vinyl phthalamide was copolymerized with methyl methacrylate, isobutyl methacrylate or butyl acrylate. The copolymerizations were initiated free radically and it was necessary to conduct the polymerizations in solution or else insoluble products would result. In most cases the polymerizations preceded to relatively high conversions in a short time. The conversions necessitated the use of high conversion methods to calculate the reactivity ratios. The N-vinyl phthalamide was found to be the less reactive monomer in all cases. As part of this study, poly(N-vinyl phthalamide) homopolymer was synthesized by free radical initiation. While the ^{1}H-NMR spectrum yield very little information concerning polymer stereochemistry, the methine carbon resonance in the ^{13}C-NMR spectrum displayed a sensitivity to polymer stereochemistry.

Introduction

For some time we have been investigating the polymerization and copolymerization behavior of vinyl heterocycles (1-5). Lately, we have been particularly interested in polymers and copolymers that contain functional groups capable of entering post-polymerization reactions. (5,6) Previous work has established that N-vinyl phthalamide moieties in homopolymers and copolymers can be converted to vinyl amine functionality through reaction with hydrazine (7-9). Earlier work has also established values for the reactivity ratios in copolymerizations of N-vinyl phthalamide with such common monomers as vinyl acetate, styrene and maleic anhydride (10-12). Copolymers with methyl methacrylate have also been reported (13) but no reactivity ratios were calculated. Therefore, we decided to investigate the copolymerization of N-vinyl phthalamide with commonly available acrylate or methacrylate monomer. Additionally, we decided to investigate the stereochemistry of free radical initiated poly(N-vinyl phthalamide) [PNVP] because we could find no literature reference relating to the evaluation of PNVP's stereochemistry and because we have been investigating the stereochemistry of poly vinyl heterocycles for quite some time (1-5).

Experimental

General

All solvents used in this study were reagent grade and were used without further purification. The AIBN was purified by recrystallization from methanol. The N-vinyl phthalamide was obtained from Aldrich and was purified by recrystallization from methanol. The acrylate/methacrylate monomers were purified by distillation under reduced pressure from CaH_2. Polymer spectra were recorded with a Varian Gemini 300 FT NMR on 10-15% w/v solutions of polymer in $CDCl_3$ or d_6-DMSO. The molecular weights were measured with a GPC equipped as previously described (1-5).

Copolymer Synthesis

A typical copolymerization was performed by weighing the desired amounts of comonomer into a clean, dry screw cap vial (total weight of monomers = 1.50 g), followed by 1.0 ml of dimethyl sulfoxide (DMSO). The initiator (AIBN, 0.7 wt %) was then added and the contents of the vial were sparged with dry N_2 while cold to minimize evaporation loss. The vial was then sealed with a teflon lined screw cap and placed in a thermostated waterbath (65°C) for the desired length of time. The polymerizations were terminated by removing the vial from the bath, cooling to ambient temperature and adding 5 ml of CH_3OH. The copolymers were purified by reprecipitation from $CHCl_3$ solution into CH_3OH, a process that was repeated 3 times. The copolymers were dried in vacuo at 25°C for 72 hr, then weighed to determine conversion.

Homopolymer Synthesis

N-Vinyl phthalamide (2.0 g) was weighed into a clean, dry screw cap vial. Dimethyl sufoxide (2.0 ml) was added followed by 0.75 wt % AIBN. The solution was sparged with dry N_2 and the vial was sealed with a teflon lined screw cap. The vial was maintained in a thermostated water bath at 65° for 3 hr. The polymerization was terminated by removing the vial from the bath, cooling to room temperature, and adding 5 ml of benzene. The polymer was purified by reprecipitating it four times from DMSO into benzene. The polymer was then dried for 80 hr at 30°C. Conv. = 37.7%, M_n = 82000, M_w = 149600, M_w/M_n = 1.82.

Results and Discussion

The results obtained in the copolymerization experiments are summarized in Table 1.

The data in the Table shows that moderately high conversions were obtained relatively rapidly. The use of DMSO as a solvent was necessary, otherwise crosslinked, insoluble products were obtained.

All the copolymers were obtained as white powders that had monomodal GPC traces. The homopolymer of NVP was not soluble in $CHCl_3$, however, all the copolymers produced in this work were readily and totally soluble in $CHCl_3$, indicating that true copolymers have indeed been formed.

The conversions obtained made the use of high conversion methods to calculate reactivity ratios a necessity (14, 15). These methods employ the integrated form of the Mayo-Lewis equation (conversion is accounted for) to calculate reactivity ratios. The results of these calculations are presented in Table 2.

TABLE 1

Copolymerization Results

Polymer	M_1	M_2	M_f of M_1 in Feed	PZN Time (h)	% Conv.	M_n	M_w	M_w/M_n	M_f of M_1 in Copolymer	M_f of M_2 in Copolymer
VPhM1	NVP[a]	MMA	0.06	1.0	45.8	61000	121000	1.98	0.02	0.98
VPhM2	NVP	MMA	0.15	1.0	34.6	88000	161000	1.83	0.05	0.95
VPhM3	NVP	MMA	0.22	1.0	34.1	77600	14600	1.88	0.08	0.92
VPhM4	NVP	MMA	0.34	1.0	37.2	83300	16600	1.99	0.13	0.87
VPhM5	NVP	MMA	0.39	1.0	31.7	56500	102500	1.81	0.17	0.83
VPhM6	NVP	MMA	0.54	1.0	47.7	56000	88000	1.57	0.30	0.70
VPhM7	NVP	MMA	0.61	1.0	36.5	58300	104000	1.78	0.33	.067
VPhM8	NVP	MMA	0.73	0.75	33.6	62200	117000	1.88	0.48	0.52
VPhI1	NVP	IBMA	0.13	0.75	20.4	95000	174000	1.83	0.05	0.95
VPhI2	NVP	IBMA	0.22	0.75	21.5	86000	145000	1.69	0.09	0.91
VPhI3	NVP	IBMA	0.26	0.75	21.5	98000	175000	1.79	0.11	0.89
VPHI4	NVP	IBMA	0.51	0.75	22.3	97500	185000	1.90	0.22	0.78
VPhI5	NVP	IBMA	0.66	0.75	30.6	83500	142000	1.70	0.37	0.63
VPhI6	NVP	IBMA	0.76	0.75	28.3	67200	124000	1.85	0.46	0.54
VPhB1	NVP	BA	0.07	0.75	17.9	210000	393000	1.87	0.06	0.94
VPhB2	NVP	BA	0.15	0.75	33.9	535000	806000	1.51	0.14	0.86
VPhB3	NVP	BA	0.23	0.75	34.2	302000	505000	1.67	0.21	0.79
VPhB4	NVP	BA	0.35	0.75	48.4	260000	485000	1.87	0.32	0.68
VPhB5	NVP	BA	0.50	0.75	23.8	133000	259000	1.95	0.39	0.61
VPhB6	NVP	BA	0.63	0.75	9.8	118000	185000	1.57	0.45	0.55

a) NVP = N-vinyl phthalamide; MMA = methyl methacrylate; IBMA = isobutyl methacrylate; BA = butyl acrylate

TABLE 2

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
NVP	MMA	0.21 ± .01	3.97 ± .3	0.83
NVP	IBMA	0.12 ± .02	3.41 ± .7	0.41
NVP	BA	0.13 ± .01	0.86 ± .09	0.11

TABLE 3

Average Sequence Lengths

Polymer	M_1	M_2	$_1$[a]	$_2$
VPhM1	NVP	MMA	1.00	195.53
VPhM3	NVP	MMA	1.02	46.66
VPhM6	NVP	MMA	1.09	10.26
VPhM8	NVP	MMA	1.19	5.30
VPhI1	NVP	IBMA	1.01	65.79
VPhI3	NVP	IBMA	1.02	28.59
VPhI6	NVP	IBMA	1.10	5.00
VPhB1	NVP	BA	1.01	14.00
VPhB3	NVP	BA	1.03	4.12
VPhB6	NVP	BA	1.11	2.01

a) $_1$ = average sequence length of M_1; $_2$ = average sequence length of M_2

Average sequence lengths for several of the copolymers synthesized in this study were calculated using Pyun's equations (16), the results of these calculations are summarized in Table 3.

The reactivity ratios and average sequence lengths show that growing chains much prefer to add the acrylate or methacrylate comonomer no matter what the terminus is. Butyl acrylate monomer is the nearest in reactivity to the NVP with high levels of feed NVP (VPhB6) yielding copolymers with some alternating tendency.

As previously stated we could find no references as to assessment of the stereochemistry of NVP homopolymers. In addition, we have been studying the stereochemistry of free radical initiated polyvinyl heterocycles for quite some time and have noted that attachment of the vinyl group to atoms other than carbon can lead to interesting effects in the nmr spectra of the resulting polymers. Therefore, we decided to investigate the nmr spectra of poly(N-vinyl phthalamide) initiated via free radical means.

The 300 MHz proton spectrum revealed no resonances that showed sensitivity to polymer stereochemistry so no analysis was possible.

The ^{13}C-NMR spectrum of PNVP along with a linear expansion of the methine carbon resonance is in Figure 1. The resonances are assigned as shown in the Figure (17, 18). The carbonyl and ring carbon resonances appear as single broad peaks devoid of any fine structure which would indicate a sensitivity to polymer stereochemistry.

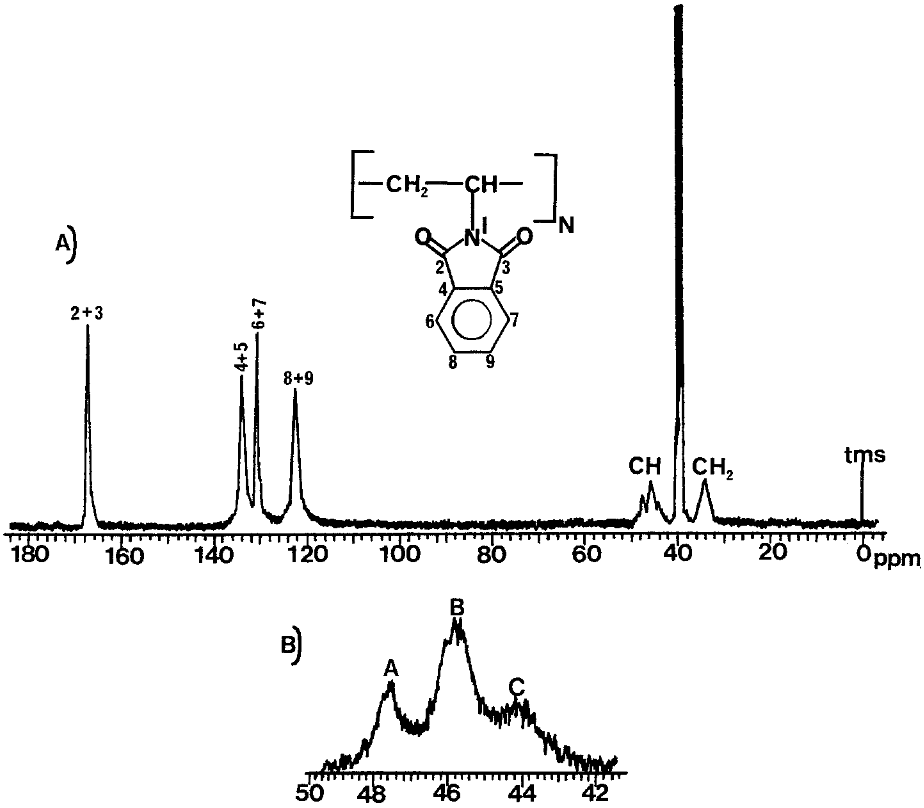

Figure 1

^{13}C-NMR Spectrum of PNVP: A) Full spectrum
B) Methine carbon resonance

In fact, the only resonance showing any multiplicity indicating sensitivity to polymer stereochemistry is the methine carbon resonance. The methine carbon resonance (Figure 1B) occurs as a three peak pattern in a relative intensity ratio of 1:2:1, A:B:C. This is the relative intensity ratio expected for the triads of an atactic polymer. Calculation of a P_m value from the fractional intensity of peak A (0.25 ± .04) yields $P_m = 0.50 \pm .08$. Previous work (5 and references therein) has indicated that a reasonable assignment in terms of triads is A = mm, B = mr + rm and C = rr. These results suggest that PNVP is an atactic polymer when synthesized under the conditions used in this work.

Conclusions

The free radical copolymerization behavior of NVP as well as the stereochemistry of NVP free radical initiated homopolymer has been investigated. In most cases the copolymerizations proceeded rapidly to moderately high conversions. The conversions obtained made it necessary to use high conversion methods in the calculation of reactivity ratios. Additionally, the rate of the polymerization made the use of a solvent necessary in order to moderate the reaction and so soluble products could be obtained. In all cases the NVP proved significantly less reactive than the acrylate or methacrylate comonomer with long sequences of these monomers being produced even at relatively high levels of NVP in the feed.

The only resonance in the ^{1}H- or ^{13}C-NMR spectra that showed any discernible sensitivity to polymer stereochemistry was the methine carbon resonance. Analysis of this resonance showed a pattern that could be assigned in terms of triads for an atactic polymer.

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