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Study of radical copolymerization of 4-chloro-3-nitrostyrene with vinyl monomers

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Results of the copolymerization of 4-chloro-3-nitrostyrene (4-CNS) with acrylic and vinylic monomers in bulk or in solution are reported together with some related physico-chemical characterizations, i.r. and n.m.r. data, d.s.c., and solubility properties. These experiments allowed us to characterize the high reactivity of 4-CNS and its main effects (inhibition or retardation) on the copolymerizations studied. In all cases, and more particularly with methacrylic derivatives, copolymerization proceeded slowly, and at limited conversion rates; the copolymer compositions reveal preferential incorporation of 4-CNS. For methyl methacrylate copolymerization no significant induction time was detected, indicating a retarding effect on the kinetics due to 4-CNS. © 1997 Elsevier Science Ltd.

(Keywords: nitrostyrene derivatives; radical copolymerization; retarding effect)

INTRODUCTION

Owing to the interest in *ortho* halogeno–nitrobenzene structures for the manufacture of synthetics, studies of various halogenated nitrostyrenes[1–3] have been carried out. These styrene derivatives could lead to the formation of heterocyclic moieties, such as benzimidazole methanethiol or benzimidazole methanol groups attached to a polymeric backbone[4], and, as a result, polymeric reagents or catalysts useful in several fields[5,6] could be obtained. However, these nitro derivatives originally appeared to play a particular role in radical polymerization, either an inhibiting or a retarding one[7,8], which had not been extensively studied at that time.

The study of substituted nitrostyrene polymerization began early in the 1940s, and was not always successful. For instance, Marvel *et al.*[9] reported that 3-nitrostyrene did not polymerize when treated in bulk with benzoyl peroxide, whereas others, such as Wiley and Smith[10], reported that its copolymerization is very slow with benzoyl peroxide compared to styrene or 4-nitrostyrene; indeed, the polymerization of 4-nitrostyrene is described by Wiley and Smith[11] as 'rapid', which explains why its copolymerization was more extensively studied.

Concerning the copolymerization of nitrostyrenes, it was first reported that 3-nitrostyrene does not copolymerize with butadiene in bulk, whereas in solution, with other vinyl monomers (i.e. styrene, methyl methacrylate or parachlorostyrene), copolymers can be obtained with very low yields (< 10%) and molecular weights (< 2000)[12]. On the other hand, Wiley and Behr[13] reported that 2,4,6-trinitrostyrene did not copolymerize in any way, and in fact behaved as a polymerization inhibitor.

It is difficult to find later descriptions of the radical polymerization of nitrostyrenes, and subsequent researches were oriented towards charge transfer complex[14] or anionic polymerization[15]. Nevertheless, a new series of fundamental studies on radical polymerization of substituted styrenes (nitro-, chloro- and bromo- derivatives) started in the 1980s[16–18], and this work is an original contribution to this field.

METHOD

4-CNS was synthesized from 4′-chloroacetophenone (Aldrich) as described elsewhere[1], and purified by liquid chromatography on a silica column, using benzene as the eluant. The following monomers (from Aldrich or Fluka) were purified by vacuum evaporation on a cold condensing surface: methacrylonitrile (MAN), methacrylic acid (MAA), *n*-butyl acrylate (BA), 1-vinyl-2-pyrrolidinone (VP), acrylic acid (AA), N,N-dimethyl acrylamide (DMA), vinyl acetate (VA), methyl methacrylate (MMA) and acrylamide (AAm). Once purified, all monomers were stored at −10°C under an inert atmosphere before use. Dimethylformamide (DMF purum from Aldrich) used for the solution polymerization was purified by distillation.

The azo-nitrile initiators used, 2,2′-azo-bis-isobutyronitrile (AIBN from Aldrich) and 2,2′-azo-bis-(2,4-dimethylvaleronitrile) (ADVN from Polysciences), were recrystallized from cold methanol solutions at ~ 10°C. All the other chemicals and solvents needed, which were available on the market, were used as received without further purification.

General polymerization procedure

The bulk and solution polymerizations were carried out under magnetic stirring in a small glass reactor within the temperature range 40–70°C. The total weight of monomers used was approximately 5 g, diluted with

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5 ml of solvent in the case of solution polymerization. The reaction mixture was deoxygenated by three freeze–thaw cycles. The initiator was then introduced under an argon blanket and the temperature controlled with a thermostatted oil bath. At the end of the reaction time, the reaction mixture was cooled to room temperature and small amounts of solvent (usually acetone) were added to dissolve the polymer or, in some cases, to lower the viscosity of the product and ease its recovery from the reactor. Purification was performed by re-precipitation of the solution obtained in a non-solvent able to dissolve the unreacted starting monomers; in the case of solution polymerization, the solvent was first partly evaporated under reduced pressure at room temperature before being poured into the non-solvent suitable for precipitation.

Characterization and analytical methods

The solubility properties of each copolymer were carefully determined and compared to those of the homopolymers; whenever possible, a combination of solvent and non-solvent was used to purify the samples from the presence of homopolymers. The copolymers were characterized by infrared–red spectra (recorded on a Bruker IFS 125 spectrometer) and ^{13}C n.m.r. spectra (recorded on a Bruker AC 200P) (*Table 1*). Their compositions were determined by elementary analysis of chlorine (Service Central d'Analyses—CNRS, Vernaison, France) as well as from their ^{13}C n.m.r. spectra, after careful purification via adequate solvent–non-solvent reprecipitation. Intrinsic viscosities (η, ml g^{-1}) were extrapolated from measurements carried out from DMF solutions at 25°C. The glass transition temperatures (T_g, °C), defined as the value corresponding to a 50% variation of the signal, were measured by differential scanning calorimetry on a Setaram apparatus (DSC-92) with heating rates of 10° min^{-1}; the data reported were corrected for thermal lag by appropriate calibration curves. Density measurements were performed with a helium pycnometer (ACCUPYC 1330 apparatus).

RESULTS AND DISCUSSION

4-CNS/MMA copolymerization conditions

The ability of 4-CNS to copolymerize was first tested with methyl methacrylate (MMA). Several parameters were studied: monomer ratio, initiator type and concentration, solvent amount, temperature. These preliminary tests have been carried out to their maximum of polymerization (reaction times up to 48 h) and enabled us to ascertain that copolymers could be readily prepared; their yield, composition and limiting viscosity number were markedly influenced by the reaction parameters.

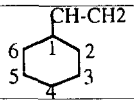
Influence of 4-CNS/MMA monomer ratio

As the mole fraction of 4-CNS was increased with respect to MMA, both the yield and limiting viscosity index of the copolymer sharply decreased, especially for lower values of 4-CNS (*Figure 1*), together with preferential incorporation of the nitro monomer. Recalling that in the same conditions the exothermic MMA homopolymerization proceeds within a few seconds, the strong influence of 4-CNS as an inhibitor or retarder can be clearly seen. Taking into account these preliminary results, the ability of 4-CNS to copolymerize has been studied with a 4-CNS monomer mole fraction (f_1) limited to 0.25.

Influence of initiator concentration and reaction temperature

The effects of temperature and initiator concentration on yield and intrinsic viscosity were first studied with 2,2′-azo-isobutyronitrile (AIBN) (*Table 2*). The main effects within the domain studied revealed that the quantity of initiator has a marked effect on yield as well

Table 1 4-CNS copolymers: ^{13}C n.m.r. spectroscopy identification

		Carbon atom number								
		C1	C2	C3	C4	C5	C6		CH	CH$_2$
4-CNS^a		138.2 s	123.4 d	148.5 s	126.1 s	132.4 d	131 d		134.1 d	118 t
Poly 4-CNS^a	1.0	145.0	123.0	147.0	125.0	131.6	133.4		30.1	23
Copolymers	F_1^{c}	C1	C2	C3	C4	C5	C6	C=O	C aliphatic	
Co-MMA^a	0.3	145.0	125.5	147.5	122.8	132.2	133.9	173.8	58 to 19	
Co-DMA^b	0.61	144.3	125.1	148.0	125.1	132.4	132.4	174.1	45 to 24	
Co-BA^b	0.55	144.0	125.5	148.2	125.5	132.5	132.5	174.8	65 to 13	
Co-AA^a	0.66	145.1	125.2	147.5	123.3	131.7	133.5	176.4	26 to 22	
Co-MAA^a	0.33	147.2	125.9	147.6	123.1	131.5	134.4	178.4	65 to 15	
Co-MAN^{a,d}	0.38	145.1	125.8	147.8	123.9	132.0	134.1		47 to 22	
Co-AAm^a	0.74	145.4	125.2	147.3	123.0	131.6	133.3	176.3	25 23	
Co-VA^a	0.92	145.2	125.2	147.4	123.1	131.6	133.3	170	27 24	
Co-VP^a	0.35	147	126	147	123.5	131.2	134.5	179	26 to 16	

^{a} In DMSO D6
^{b} In CDCl$_3$
^{a} F_1 determined from n.m.r. spectra
^{d} δ CN = 123.9 ppm
s: singlet; d: doublet; t: triplet; F_1: 4-CNS mole fraction in copolymer

MAA: methyl methacrylate
DMA: dimethyl acrylamide
MAN: methacrylonitrile
AA: acrylic acid
BA: butyl acrylate
VA: vinyl acetate
MAA: methacrylic acid
AAm: acrylamide
VP: 1-vinyl 2-pyrrolidinone

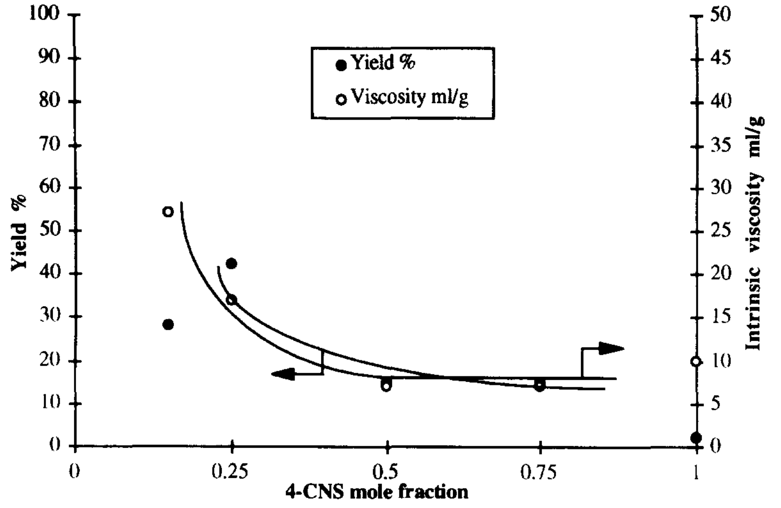


Figure 1 Effect of 4-CNS mole fraction on 4-CNS–MMA bulk copolymerization at 60° (AIBN = 0.44 mol%)

Table 2 Bulk copolymerization of 4-CNS with MMA using AIBN. Reaction time: 48 h. AIBN = 2,2′-azo-bis-isobutyronitrile. Monomer feed: 4-CNS ≈ 7 mmol, i.e. monomer feed weight fraction $f_1 = 0.25$

Test No.	T (°C)	Initiator (mol %)	Yield (%)	η (ml g^{-1} DMF) at 25°C	4-CNS mole fr. F_1 in copolymer
1	60	0.44	41	17	0.38
2	60	0.88	59	28	0.35
3	70	0.44	43	14	0.38
4	70	0.88	68	34	0.33
5	70	1.32	85	24	0.38

as on intrinsic viscosity, both at 60° and 70°C, whereas the 4-CNS mole fraction in the copolymer (F_1) was almost steady. The influence of the initiator increase can be better shown by plotting the data in the form of adimensional coordinates, as shown in *Figure 2*, and the similarity of the yield increase is striking: a three-fold increase of the initial amount of initiator at 70°C, i.e. from 0.44 to 1.32 mol%, resulted in double the yield with a viscosity increase of about 40%, a similar trend being also observed at 60°C. These features, clearly linked with the higher amount of radicals produced per unit time, are not common in classical copolymerization; usually the yield is not so strongly linked with the initiator level whereas the viscosity, conversely, decreases with higher amounts of radicals.

In order to confirm these first trends, another initiator has been used, 2,2′-azo-bis-2,4-dimethyl valeronitrile (ADVN), whose half-life calculated from reported data[19] is markedly shorter at 60°C, thus yielding more radicals under these conditions. As expected, the yields obtained with ADVN at 60°C were better (73%) than with AIBN (59%), with similar viscosity values (*Table 3*). For these reasons ADVN was preferred as an initiator for the following copolymerization experiments.

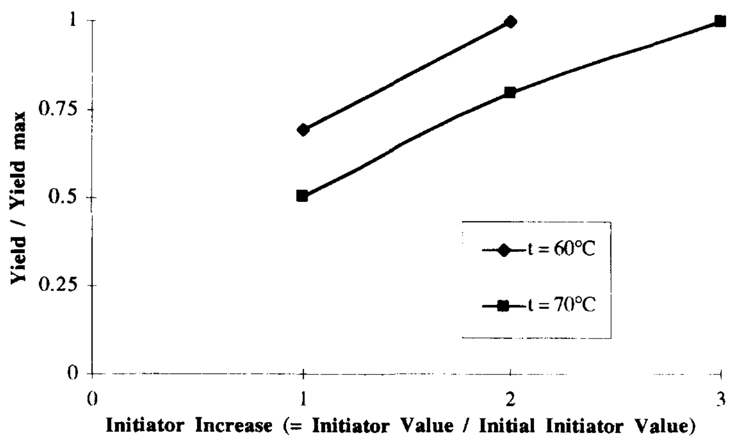


Figure 2 Comparative effect of the amount of initiator (AIBN) on bulk copolymerization of 4-CNS and MMA at 60°C and 70°C

Table 3 Bulk copolymerization of 4-CNS with MMA using ADVN. ADVN = 2,2′-azo-bis-2,4-dimethylvaleronitrile, 0.88 mol%/monomers. Monomer feed: 4-CNS ≈ 7 mmol. Comonomer = 21 mmol

Test No.	T (°C)	Reaction time (h)	Yield (%)	η (ml g^{-1} DMF) at 25°C	4-CNS mole fr. F_1 in copolymer
1	60	48	73	25	0.29
2	50	48	79	33	0.29
3	40	48	56	26	0.37
4[a]	50	48	18	9	1
5	50	2	7		0.45
6	50	4	14		0.45
7	50	6	19		0.43
8	50	8	26		0.42

[a] Homopolymerization of 4-CNS; $M_w = 16400$ from s.e.c. measurements

Polymerization temperature

The use of ADVN allowed us to work at lower polymerization temperatures, i.e. 50°C and 40°C. As pointed out before, ADVN is more adapted to lower temperatures because it ensures a more abundant generation of free radicals than AIBN; in fact, at 50°C, the half-life of ADVN in toluene is 13 h whereas that of AIBN is about 110 h[20]. With this set of conditions, an enhancement of the yield and intrinsic viscosity was obtained, the maximum value being reached at 50°C (*Table 3*). From the experiments carried out with AIBN and ADVN, one can compare the results obtained respectively at 60 and 50°C, where the number of radicals produced in a given time is roughly the same; it appeared that a higher yield was reached at the lower temperature whereas the limiting viscosity numbers remained almost steady. The comparison demonstrates the particular behaviour of 4-CNS.

Copolymerizing of 4-CNS with other monomers

The scope of the ability of 4-CNS to copolymerize was further investigated with other organosoluble monomers, namely methacrylonitrile (MAN), *n*-butyl acrylate (BA) and vinyl acetate (VA), and also with other water-soluble monomers, namely acrylic acid (AA), methacrylic acid (MAA), N,N-dimethyl acrylamide (DMA) and 1-vinyl 2-pyrrolidinone (VP); all these monomers of various solubility parameters are known for their copolymerization ability. After their formation, the copolymers were isolated and purified in the light of their solubility properties (*Table 4*).

Bulk copolymerization. When carried out under the same conditions, the experiments led to fair or rather low yields (from 51% down to 15%), except in the cases of MAA and MAN, where the yields were 79 and 66% respectively. For each of these new copolymers, the 4-CNS mole fraction incorporated is higher than the one used in the initial monomer mixture ($f_1 = 0.25$), as observed also for MMA copolymerization, meaning that the reactivity of 4-CNS is higher than all the other comonomers tested here. In most of the cases, the intrinsic viscosity data were well above the 4-CNS homopolymer data, indicating that the ratio of propagation to termination reactions is increased as a consequence of a higher rate of propagation reaction.

Solution copolymerization. The same main trends already seen for bulk copolymerization were found in an aprotic polar solvent such as N,N-dimethylformamide (DMF); on the other hand, the use of methanol or benzene gave poor results. The yields reached in DMF were the same or even higher than those obtained in bulk, whereas the copolymer compositions were close to those obtained in bulk copolymerization, stressing again the high reactivity of 4-CNS; nevertheless, a comparison of the intrinsic viscosities recorded for each type of conditions indicated lower values for experiments carried out in solution. In the case of MMA copolymerization, the improved yield (up to 90%) could be explained by an enhanced reactivity of MMA with respect to 4-CNS, due to the solvent via a charge transfer complex mechanism. Indeed, some authors have already pointed out that MMA can form such a complex[20], the concentration of which depends on the nature of the solvent used. An overview of these results is presented in *Table 5*, where both bulk and solution copolymerization data have been gathered.

Copolymer characterizations

The molar fraction of 4-CNS incorporated (F_1) in copolymers, reported in *Table 4* (from chlorine analysis) and *Table 1* (from n.m.r. analysis), exhibited very good agreement for most of the samples. The n.m.r. carbon peak assignments were made quite easily with the help of pure monomer or polymer spectra as references, except for CNS-VP copolymer where five small non-identified peaks were found, and for CNS-VA due to the low VA content. As a general feature, the chemical shifts of the aromatic CNS ring were almost unchanged in copolymers with respect to the poly(4-CNS) spectra. The i.r. characterizations recorded (*Table 6*) were also well consistent with the expected ones.

Glass transition temperatures (T_g, °C) and the corresponding variations of specific heat capacity (ΔC_p, J(g K^{-1})) have been obtained for most of these new materials from d.s.c. experiments, carried out with well-dried samples at room temperature under vacuum (*Table 7*). At least three heating/cooling cycles were recorded; most of the time, the first cycle curves were rather different from the following ones because of the thermal history of the samples, and the glass transition was increased by about 2–5°C in subsequent cycles. The T_g values of poly(4-CNS) varied with the method of synthesis used (*Table 7*); not detected for samples of low viscosity prepared in bulk ($\eta \approx 5$ ml g^{-1} in DMF at 25°C), they are in the range 114–119°C for samples prepared in solution with a low amount of initiator

Table 4 Solubility properties of 4-CNS copolymers

Copolymer (Homopolymer)	4-CNS mole fr.[a]	Solvent	Non-solvent
4-CNS–MMA	0.29	[b] acetone	[b] MeOH
(4-CNS)	1	acetone, THF, DMF, pyridine	MeOH, Et_2O, $CHCl_3$, toluene
(MMA)	0	$CHCl_3$, toluene	MeOH, Et_2O, CCl_4
4-CNS–MAN	0.38	[b] acetone, $CHCl_3$, DMF	[b] Et_2O, EtOH, benzene
(MAN)	0	DMF, pyridine	H_2O, EtOH, Et_2O, $CHCl_3$
4-CNS–BA	0.54	[b] acetone, $CHCl_3$, DMF	[b] Et_2O, MeOH
(BA)	0	acetone, THF, benzene	Et_2O, MeOH
4-CNS–VA	0.92	[b] acetone	[b] MeOH
(VA)	0	MeOH, acetone, THF, $CHCl_3$	EtOH (anhydrous)
4-CNS–MAA	0.3	[b] MeOH, hot H_2O	[b] Et_2O, acetone
(MAA)	0	H_2O, MeOH	EtOH, acetone
4-CNS–VP	0.31	[b] acetone	[b] i. PrOH, $i.Pr_2O$
(VP)	0	EtOH	acetone, CCl_4, $i.Pr_2O$
4-CNS–AA	0.5	[b] MeOH, acetone	[b] Et_2O
(AA)	0	H_2O, MeOH, DMF	Et_2O, acetone
4-CNS–AAm	0.46	[b] acetone	[b] H_2O, MeOH
(AAm)	0	H_2O	EtOH
4-CNS–DMA	0.58	[b] acetone	[b] MeOH
(DMA)	0	H_2O, MeOH	Et_2O

[a] Copolymer composition determined from elemental analysis of chlorine

[b] Solvent/non-solvent used to recover the polymers from bulk and solution polymerizations

Table 5 Copolymerization of 4-CNS with bulk or solution conditions. Reaction conditions: 48 h at 50°C; ADVN: 2,2′-azo-bis-2,4-dimethylvaleronitrile, 0.88 mol%/monomers. Monomer feed: 4-CNS ≈ 7 mmol, i.e. 4-CNS mole fraction: $f_1 = 0.25$

Test No.	Comonomer with 4-CNS	Yield (%) bulk	Yield (%) solut.	η (ml g^{-1} DMF at 25°C) bulk	η (ml g^{-1} DMF at 25°C) solut.	4-CNS mole fr. F_1 in copolymer bulk	4-CNS mole fr. F_1 in copolymer solut.	Solvent used, weight %
1	methyl methacrylate	79	90	33	20	0.29	0.26	DMF, 61
2	methacrylonitrile	66	66	44	15	0.37	0.37	DMF, 61
3	butyl acrylate	38	51	13	13	0.54	0.49	DMF, 56
4	vinyl acetate	12	—	4	—	0.92	—	
5	methacrylic acid	51	54	55	17	0.30	0.37	DMF, 62
		—	6	—	15	—	0.45	MeOH, 50
6	1-vinyl-2-pyrrolidinone	23	0	53	—	0.31	—	benzene, 75
7	acrylic acid	18	—	—	—	0.50	—	
8	dimethyl acrylamide	15	—	8	—	0.58	—	
9	acrylamide	—	32	—	10	—	0.46	DMF, 64
Ref.:	homopoly(4-CNS)	18	19	9[a]	5[a]	1		

[a] From s.e.c. measurements: in bulk, $M_w = 16400$; in solution, $M_w = 7400$

(< 1 mol%) up to 130–132°C for higher amounts. For 4-CNS polymer prepared in emulsion according to a procedure reported previously[2], the T_g is even higher, up to 134°C; this wide T_g range may well be due to the formation of small chains trapped into the polymer and difficult to eliminate on account of the poor solubility of the chloro-nitro structures. In the literature, the values given for poly(4-chlorostyrene) and poly(4-nitrostyrene) are respectively 133°C[21] and 194.6°C[22]. The copolymers prepared exhibited a single glass–rubber transition (*Table 7*); the general trend indicates that the T_g is strongly increased by the incorporation of 4-CNS residues in the copolymer structure, this increase being far higher than the one expected from a simple calculation of the copolymer T_g using a Fox[23] type relation:

$$1/T_{g\,\text{Copoly A–B}} = \text{weight fraction}_A/T_{gA} + (1 - \text{weight fraction}_A)/T_{gB},$$

with T_g in K.

Kinetic study of 4-CNS–MMA copolymerization

It was of interest, in the case of this particular nitrostyrene, to investigate whether its role, i.e. its behaviour as an inhibitor or retarder, could be clearly identified. In order to gain more insight into such an effect, a number of copolymerizations of 4-CNS with MMA have been carried out at 50°C with 0.88 mol% of

Table 6 4-CNS copolymers: *FT*i.r. spectroscopy identification ($\bar{\nu}$, cm^{-1})

I.r. bands	Poly4-CNS	Co-VP	Co-MMA	Co-MAN	Co-BA	Co-AAm	Co-DMA	Co-MAA	Co-AA
CH_2 asym	2927.5	2929.2	2993.3	2981.9	2950	2928.2	2927.2	2991.6	2929.7
NO_2 asym	1533	1534	1537	1535	1535	1532	1534	1535	1533
NO_2 sym	1351	1352	1354	1352	1352	1351	1352	1353	1351
C–NO_2	832.5	832.9	836	832.7	832.4	833.1	833.6	830.2	833.1
C=C arom	1604	1603	1600	1605	1604	1603.9	fused	fused	1605
C=C arom	1478.7	1478.8	1479.8	1479.3	1478.9	1478.8	1479.2	1479.7	1479.1
C–H arom^a	1135	1136		1135		1135	1137	fused	1137
C–H arom^a	897	896	896	895	895.1	896	895	897	896
Carom-Cl	1050	1050	1050.1	1050.1	1050.1	1049.9	1049.9	1050.4	1050.1
C=O		1684.7	1720		1720	1678.8	1637.7	1705	1731/1707
Particular bands			C–O–C 1148	–CN 2233.2	C–O–C 1164	$CONH_2$ 3470–3389	$CONH_2$ 3454	CO_2H 3480/963	CO_2H 3427

^{a} 1,2,4-trisubstituted aromatic ring

Table 7 D.s.c. data for 4-CNS polymers. F_1: 4-CNS mole fraction in the copolymer

Poly 4-CNS^a from:		Bulk		Solution:		Init.%: < 1 or > 1		Emulsion	
T_g (°C) (2nd or 3rd cycle):		no T_g detected				119	131.8	134	
ΔC_p (J (g K)$^{-1}$)						0.17	0.16	0.17	
Copoly 4-CNS	with	BA	VP	DMA	MMA^a	MAN	PAA	MAA	AAm
Homopolymers^b	T_g (°C)	−54	54	89	126	120	106	228	165
Composition:	F_1:	0.54	0.31	0.58	0.29	0.37	0.5	0.3	0.67
	T_g (°C)	59.9	145.8	143.2	128.3	146.5	160	177.3	158
	ΔC_p (J (g K)$^{-1}$)	0.11	0.15	0.18	0.2	0.21	0.26	0.25	0.15
Calculated T_g (°C)^c		24.8	74.29	101.1	117.2	111.3	106	161.3	114.4

^{a} Density (25°C) = 1.45 for poly(4-CNS) = 1.31 for poly(4-CNS–MMA)

^{b} According to this work or literature data[21]

^{c} Fox equation (cf. ref. 23)

ADVN as initiator and stopped in their early stages at relatively low conversion values, the yields then being carefully determined as well as the related copolymer compositions. In these conditions, it was found that within the first hours of the reaction, the copolymer composition was almost constant and demonstrated a strong and steady enrichment in 4-CNS (*Table 3*, runs 5–8). Hence, it was reasonable to assume that the propagation reaction proceeds according to steady-state conditions, and one could analyse these results following the simplified kinetics generally proposed for an overall apparent polymerization rate:

$$R_p = -d[M]/dt = k_{1app}.[M] \qquad (1)$$

where $[M]$ and k_{1app}. represent respectively the monomer concentration and the first-order apparent polymerization rate.

$[M]$, which can also be approximately expressed as equal to $[M_0] - [M$ consumed monomer$]$, is proportional to $P_t - P$, where P_t is the total theoretical amount of polymer that can be formed and P is the weight of polymer formed at time t. Substituting $[M]$ in equation (1):

$$d(P)/dt = k_1'(P_t - P) \text{ or } dP/(P_t - P) = k_1' \, dt \qquad (2)$$

Integration of equation (2) gives a linear expression of polymer formation *versus* time:

$$Y = -\ln[1 - (P/P_t)] = k_1' t \qquad (3)$$

where P/P_t indicates the conversion rate at a time t. As stated before, the copolymer composition was almost steady in the early stages of the reaction, and therefore the weight variations (P/P_t) can be reasonably used instead of the concentration variations of the monomers.

Despite the conversion values, which are already high to fulfil strictly the assumption of initial steady state, it can be seen from *Figure 3* that the experimental data obtained for the 4-CNS copolymerization can be well fitted by a linear curve going through the origin up to a conversion value of 26%. The corresponding equation is $Y = 1.02 \times 10^{-5}\, t - 0.001$ (determination coefficient $R = 0.997$; 5 points), the slope being thus the apparent first-order rate constant, i.e. $k_1' = 1.02 \times 10^{-5}\,s^{-1}$. The related kinetic plots of bulk polymerization of 3-CNS and 4-CNS (for analogous conditions: 1 mol% ADVN at 51°C), previously reported[3], are presented for comparison in *Figure 3*; interestingly, linear fitting of the experimental points can obviously be made, the straight lines also passing almost through the origin (respective slopes k_1': 2.1×10^{-5} and $3.8 \times 10^{-6}\,s^{-1}$). As one might expect, the apparent rate constant value of the copolymerization is well above the one corresponding to the bulk polymerization of 4-CNS (~ 2.7 times higher). In the early stages of the reaction, these results indicated a

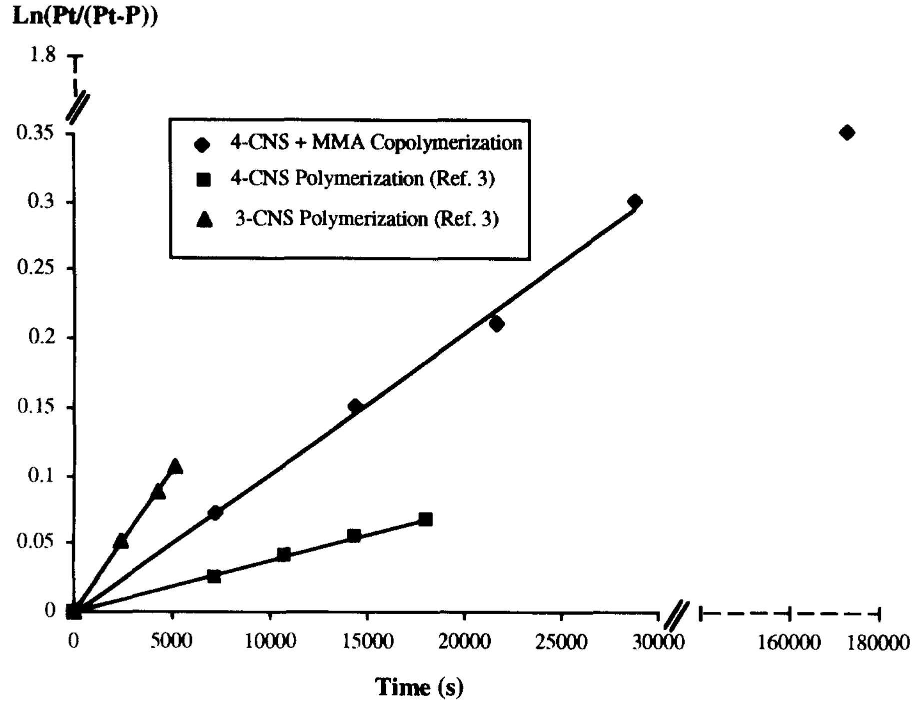


Figure 3 4-CNS–MMA copolymerization vs time: $\ln[P_t/(P_t - P)] = k'_1 t$ (ADVN = 0.88 mol%, T = 50°C). Comparison with 3-CNS and 4-CNS polymerizations

first-order reaction, characteristic of a non-inhibited polymerization; indeed, the calculated times of the start of polymerization, i.e. when the yield is 0, range from 248 s (for 4-CNS–MMA copolymerization) up to 600 s (for 4-CNS homopolymerization), which are very low values, well in agreement with the experimental error, if one considers the low rate constants determined.

Taking into account the whole set of data reported in this work, the relatively high initial reactivity of 4-CNS and the long reaction times needed to achieve bulk or solution reactions, it is clear that conflicting phenomena must occur during the copolymerization reaction, giving rise to the particular results observed. Indeed, since no inhibiting effect has been detected, it seems that the 4-CNS acted more likely as a retarder; this conclusion is in agreement with the work of Foord[24], who characterized some nitro-aromatic compounds as true retarders for the thermal polymerization of styrene. To take this behaviour into account, we now propose an interpretation based on a stabilized form of the growing radical.

First, the reactivity seen for the 4-CNS monomer itself can be well understood on the basis of electron withdrawing effects of the two substituents of the aromatic ring; indeed, both of them must favour a radical addition on the vinyl bond of the styrene by decreasing strongly its electronic density. In the case of some vinyl derivatives, interesting relations of the reactivity of the double bond have also been observed and related to the Hammett constants for *para*-substituted styrenes[25]. Therefore, knowing that the overall slow reaction kinetic observed is not determined by the reactivity of the nitro monomer itself, one can deduce that the 4-CNS radical must be involved in a stabilized structure which slows the polymerization process.

One common assumption for inhibition due to nitro compounds is direct addition of radical species on the nitro group, leading to chain termination; but such a mechanism would not explain the slow kinetics observed, well in evidence for 4-CNS/MMA copolymerization. Hence, to take it into account, the assumption of the formation of a resonance stabilized radical, directly linked to the position of the nitro group on the ring, is made and represented in *Figure 4*; this corresponds to the addition of a radical species on the ring under the strong electron withdrawing effect of the nitro group. Such a radical, stabilized by the captodative effect, is too stable to act as an initiator in the polymerization reaction. Moreover, the occurrence of termination reactions by hydrogen abstraction on the attack carbon is unlikely, because this transfer is hindered by the steric bulk at this position and the reaction would remain reversible. It is worthwhile to note that a similar mechanism has already been proposed by Foord[24] and Bartlett and Altschuld[26] in the case of allyl derivatives and later by Smets and Reckers for 3-nitrostyrene[13]. When a comonomer is used, the effect of the stabilization resonance limited to the CNS units decreases, leading to enhanced copolymerization results.

CONCLUSION

Conversely to earlier literature data dealing with 3-nitrostyrene, it was found that 4-chloro-3-nitrostyrene can very well be used as a comonomer in radical polymerization, and new copolymers have been successfully prepared with a wide range of different monomers, either in bulk or in solution conditions. Generally the polymerizations proceeded slowly, the best results being obtained with methacrylic derivatives; in all cases the copolymer compositions corresponding to limited conversion rates indicate that the growing chains incorporate 4-CNS more easily.

From a kinetic study carried out with methyl methacrylate, the retarding behaviour of 4-CNS has been considered; indeed, under the conditions used, no meaningful induction time could be detected and the

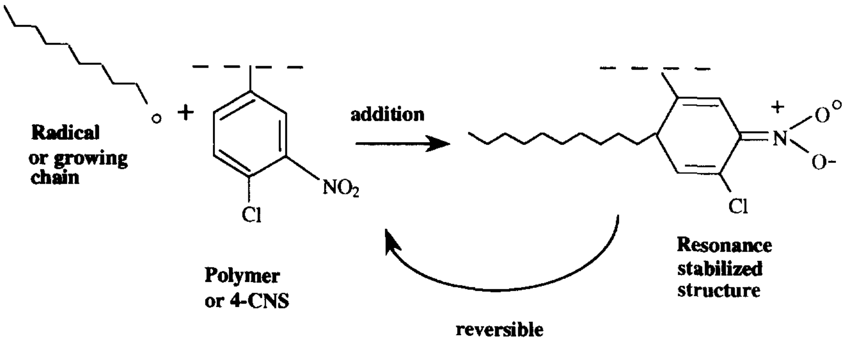


Figure 4 Formation of poorly active growing radicals

reaction course accounted for a first-order kinetic at low conversion stages. The higher molecular weight of the copolymers obtained when the nitrostyrene monomer mole fraction is low would be a consequence of the retarding character of 4-CNS.

Further studies, aiming at comparing more widely the reactivity of 4-CNS with various other vinyl monomers in radical copolymerization, will be undertaken in order to make precise and generalize, if necessary, the results obtained with MMA.

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