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Synthesis of a new styrene monomer: the 3-chloro-4-nitrostyrene

Free radical polymerization reactivity compared to 4-chloro-3-nitrostyrene

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Summary

A satisfactory synthesis route to a new monomer, the 3-chloro-4-nitrostyrene (3-CNS) is described. The results of free radical polymerisation experiments (limit of conversion, global kinetics) are reported by comparison with those of the isomer 4-chloro-3-nitrostyrene (4-CNS). They show the great influence of the nitro group position which markedly increases the reactivity of 3-CNS.

Introduction

Polymers bearing o-nitrohalogenoaromatic pendant groups are versatile precursors of various macromolecular heterocyclic structures (1). These heterocycles are then built up at the ultimate step under very simple conditions allowing thus the introduction of reactive but sensitive additional organic functional groups like a thiol. In this way polymeric reagents are accessible which display interesting properties in the field of homogenous catalysis or ionic polycomplexes.

The access of such precursor polymers is often not feasible, by chemical modification of a simple polymer like polystyrene. In fact, this route requires at least two successive reaction steps which are rather difficult to control quantitatively and regioselectively (2,3).

To be sure to introduce on each site the two substituents (halogen and NO_2) in the right position, it seems better to polymerize related monomers, the most simple being substituted styrenes such as 4-chloro-3-nitrostyrene (4-CNS)(4). The synthesis of 4-CNS can be readily achieved but, unfortunately, the first polymerisation results pointed out the difficulty to obtain rather high molecular weights (4,5). Mononitrosubstituted styrenes have been known for a long time (3-nitro, 4-nitro, 2-nitro) (6,7,8) but they have no much been studied. However, they have gained the reputation to give poor results in radical polymerisation (9), except the 4-nitrostyrene (10,11) which was subjected to patents.

The preparation of 3-chloro-4-nitrostyrene (3-CNS), the isomer of 4-CNS not yet described, was thus undertaken in order to clarify if the nitrogroup position has actually an influence on the monomer behaviour during polymerization.

We here report the results of the 3-CNS synthesis and of the first polymerisation experiments in comparison with 4-CNS.

Experimental

3-chloro-4-nitrotoluene:

Catalyst preparation for 25g of 4-amino-3-chlorotoluene : the complex catalyst (Cu_2SO_3,$CuSO_3$,$2H_2O$) was prepared by boiling a solution of $CuSO_4$,$5H_2O$ (50g) in 500ml of water and adding the required amount of sodium or ammonium sulfite to remove the blue color of the mixture. After the mixture was cooled, the precipitate was filtered off, washed with cold water and oven dried to obtain about 30g of catalyst.

Diazonium salt : a mixture of 4-amino-3-chlorotoluene (25g), sulfuric acid (d = 1.80, 10ml) and water (150ml) was cooled at 2°C. An aqueous solution of sodium nitrite (13.4g,

150ml water) was dropwise added under strong stirring so that the temperature do not exceed 12°C and then the mixture was kept at this temperature.

Nitrodediazonation : in a large sized reactor (at least 2 l) a mixture of sodium nitrite (86g) and complex catalyst (30g) in water (250ml) was cooled at -5°C and the diazonium salt solution then introduced under vigorous stirring by small successive amounts. The voluminous foam which was forming should fall before each new addition. After the addition was complete (about 2h), the mixture was stirred for 2 additional hours at the same temperature and allowed to come back to room temperature.

The copper salt precipitate was then collected in a Büchner funnel, recovered and extracted several times with ether, the last extraction being controled by TLC (silica gel, trichloroethylene,3-CNT Rf: 0.58). The aqueous solution was treated in the same way and the organic fractions were combined and the solvent was removed by rotary evaporation. The residue was purified by fractional distillation under reduced pressure (b.p: 75°C, 0.5 mm). The resulting liquid (50% yield) crystallised at room temperature, m.p: 23°C. ^1H NMR($CDCl_3$) δppm : 2.43 (s,CH_3), 7.20 (dd,H_6,$J_{6,5}$:8.30 Hz), 7.37 (d,H_2,$J_{2,6}$:0.84 Hz), 7.83 (D,H_5).

α-bromo-3-chloro-4-nitrotoluene (CNTBr):

In a two-necked flask equipped with a reflux condenser, a mixture of 3-chloro-4-nitrotoluene (8g, 1eq.), N-bromosuccinimid (9.13g, 1.1eq.) and 1,2-dibromoethane (30ml) was heated at 115°C. At this temperature 0.13g of dicumylperoxide was added and the solution stirred for 5 days. The mixture was cooled to 0°C and filtered to recover the resulting succinimid. This by-product was washed with small quantities of benzene wich were combined and added to the filtrate. After complete removal of the solvent under reduced pressure, the residue was analysed by ^1H NMR to determinate the %mol. in CNTBr.It was used as it was for the next reaction. ^1H NMR ($CDCl_3$) δppm : 4.45(s,CH_2), 7.43(dd, H_6, $J_{6,5}$: 8.42Hz), 7.59(d, H_2, $J_{2,6}$: 1.91Hz), 7.87(d, H_5).

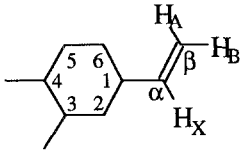
Phosphonium salt :

The operating conditions was given for a mixture containing 26g (1eq.) of CNTBr which was diluted with 50ml of acetonitrile. A solution of triphenylphosphine (55g, 2eq.) in a mixture of toluene and acetonitrile (1/1 vol., 200ml) was then added at room temperature under stirring. After 24h reaction, the precipitated solid salt was collected in a Büchner, washed with small amounts acetonitrile and oven dried at 60°C. Yield: 94-99%.The salt can be recrystallised by dissolving in hot methanol, then adding some water until solution becomes turbib and at last cooled. Mp> 200°C (decomposition). IR (KBr pellet) ν cm-1: 2760,2840,2860 (CH_2),1530 and 1360 (NO_2), 1435,1110,690,510. ^1H NMR ($CDCl_3$) δppm : 6.07 (d, CH_2, J_{CH-P}: 15.8Hz), 7.5-8 (aromatic peaks), CH_2 peaks/aromatic peaks areas ratio = 1/9. Anal. calcd. for $C_{25}H_{20}NO_2ClBrP$: C, 58.5 ; H , 3.9 ; N , 2.73 ; O , 6.24 ; Cl , 6.93 ; Br , 15.6 ; P, 6 ; found : C, 57.63 ; H, 3.85 ; N, 2.70 ; Cl, 6.84; Br, 16.58 ; P, 5.96 .

3-chloro-4-nitrostyrene :

A mixture of 37% aqueous formaldehyde solution (130ml), phosphonium salt (30g) and cyclohexane (100ml) was heated to 35°C. Then, by maintaining this temperature, 11.4g of anhydrous sodium carbonate were added (addition time about 5h) by small amounts under vigorous stirring; each quantity was added only once the red colour of the intermediate phosphorane disappeared. After the complete addition, the suspension was stirred for 1 additional hour. Then the organic layer was separated and the aqueous layer extracted with cyclohexane until no more 3-CNS remained (test by TLC). The organic fractions were combined, washed 3 times with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure giving a yellow crude oil. Vacuum evaporation (<0.1mm) on cold condensing surface (liquid nitrogen) of the stirred product at room temperature allowed to eliminate a great part of formaldehyde and as well as a TLC more eluted impurity (silica gel, benzene). The final purification was achieved by LC

(Alumina).eluted first with cyclohexane or methylcyclohexane, to eliminate the remaining impurity, and then with benzene to recover pure 3-CNS once the solvents were carefully eliminated by prolonged evaporation under reduced pressure at room temperature. Yield : 60%. The monomer must be stored in a -20°C freezer and under argon. IR (liquid) ν cm^{-1} : 1565,1575,1585 (ring and C=C), 1515 and 1335 (NO_2), 980 and 920 (vinyl).



^1H NMR (CDCl3) δppm: 5.53 (d,H_A, J_{AX}: 10.86), 5.92 (d,H_B, J_{BX}: 17.55), 6.70 (q, H_X), 7.40 (q,H_6, $J_{6,5}$: 8.45), 7.56 (d,H_2, $J_{2,6}$: 1.82), 7.90 (d, H_5).

^{13}C NMR (CDCl3): COESY ^1H-^{13}C sequences and incremental shifts (19) have been used for peak assignements : δ ppm and ^{13}C-H couplings: 119.6 (C_β,J:155.1); 125.2 (C_6,J:166.4); 126.2 (C_5,J:159); 127.5 (C_3); 129.4 (C_2,J:166.4); 133.9 (C_α,J:158.9); 143.2 (C_1); 146.5 (C_4).

4-chloro-3-nitrostyrene:

It was synthesized from 4'-chloroacetophenone in three steps with an overall yield of 81% as described elsewhere (4) with one modification: purification was achieved by two fractional distillations under reduced pressure (b.p# 80°C, < 1 mm Hg), the first one in presence of a small amount of 4-toluenesulfonic acid. Purity test by TLC (silica gel, trichloroethylene). M.p : 30°C, stable when stored under argon at -20°C.

Polymerization of 3- and 4- CNS:

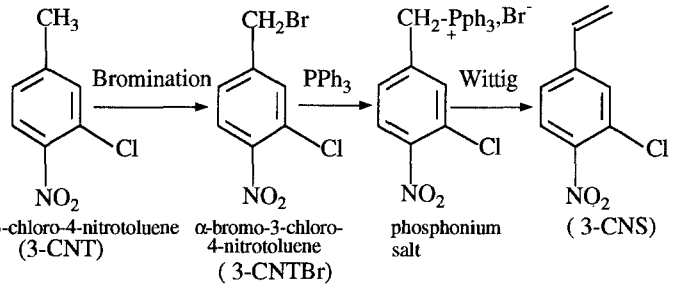
Polymerization experiments were carried out on about 2g of monomer. Monomer alone or in solution was put in tightly closed microreactor and desoxygenated by the freeze-thaw technique. Initiator ADVN was then introduced under argon sweeping, and immersed in a thermostated bath. After the proper time, the reaction mixture was very quickly dissolved in the minimum of the suitable cold solvent (DMF for 3-CNS, acetone for 4-CNS) and the polymer was precipitated by pouring the solution into an excess of a solvent of the monomer (methanol or ethanol for 3-CNS, petroleum ether or methanol for 4-CNS). The polymer was recovered by filtration, washed with the solvent of precipitation and vacuum dried at 40°C.

Poly 4-CNS : (4,5). Poly 3-CNS : IR (KBr pellet) ν cm-1: disappearance of vinyl absorptions of the monomer (especially at 1565, 920 and 980), appearance of 2830 and 2860 bands (CH_2-CH). ^1H NMR (CDCl3) : disappearance of vinyl peaks, broad peak around 1.8 ppm (CH_2-CH) Anal.calcd. for ($C_8H_6NO_2Cl$)n : C,52.32; H, 3.27; N, 7.63; O, 17.44; Cl, 19.35; found : C, 52.72; H, 3.25; N, 7.43; O, 16.68; Cl, 19.08.

Results and Discussion

I- 3-CNS synthesis :

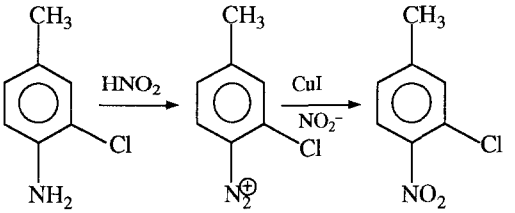
An extensive study was required in order to work out the synthesis of this new monomer. The synthetic route of its isomer 4-CNS (4), prepared in very good yield by reduction of the related acetophenone followed by dehydration of the corresponding secondary alcohol, could not be extended to the case of 3-CNS; indeed, it is very difficult to introduce in para to each other two meta orientating groups and preliminary attempts with 4-nitroacetophenone as a model have led to 4-nitrostyrene only in poor and hardly reproducible yields. On the other hand this last monomer can be prepared in excellent yield (12,13) by using the particular reactivity of phosphonium salts derived from benzylhalides; it allows to use a simplified Wittig reaction in aqueous medium. In the case of 3-CNS, it seemed suitable to take a route leading to a similar reaction according to the scheme :



However none of these three principal intermediates is commercialy available and it was necessary to reconsider (3-CNT) or to improve (3-CNTBr and phosphonium salt) their preparation taking into account the sensitivity of the activated C-Cl bond toward nucleophiles.

3-chloro-4-nitrotoluene : several ways can be considered to prepare this already known compound, but after a few attempts, the two partly described methods were not enough efficient. One (14) carries out with fairly good yield (65%) the reductive deamination of 2-amino-4-nitro-5-chlorotoluene prepared by nitration of 2-amino-5-chlorotoluene but in bad yield compared with the fluorinated homologue (15). The other, more simple in its principle, is the result of 3-chlorotoluene nitration yielding to a mixture of the two 3-4 and 3-6 isomers (16,17). Despite the use of various modified experimental conditions, the amount of 3-CNT did not exceed 30% (by ^{1}H NMR) in reaction mixture and the further separation of the two isomers either by fractional distillation or by liquid chromatography reduced strongly the yield.

Therefore we have looked for a method requiring few steps and easy to carry out. The nitrodediazonation reaction of the commercialy available 3-chloro-4-aminotoluene proved to be a short route to obtain 3-CNT in moderate yield but in pure product according to the scheme:



α-bromo-3-chloro-4-nitrotoluene: 3-CNT bromination by N-bromosuccinimide leads to a mixture of monobromo (3-CNTBr) and dibromo (3-CNTBr2) derivatives with unreacted 3-CNT. Reaction conditions were optimized by analysing the resulting mixture by ^{1}H NMR and the results showed that a moderate temperature (115°C) allows to decrease the amount of produced 3-CNTBr2 while keeping a satisfactory yield on 3-CNTBr but requires a long reaction time (4 to 5 days) and thus an initiator of low decomposition rate (dicumylperoxide). The final mixture which contains roughly 65 mole% 3-CNTBr (and 25 mole % 3-CNT, 10 mole % 3-CNTBr2) can be fractionated out by vacuum distillation but this separation is not necessary for the following step.

Phosphonium salt : the quaternary salt was synthetized by reacting the previous mixture of 3-CNTBr on an excess of triphenylphosphine. Impurities are mainly due to side reactions involving the dibromocompound; the o-chloronitro site was not involved as it was shown by lack of reaction between 3-CNT and triphenylphosphine. To avoid that drawback

mild conditions were required : low temperature and fast self precipitation of the salt. The best result was obtained by using, at room temperature, a mixture of polar and apolar solvents (acetonitrile/toluene 60-40) from which a pure salt quantitatively precipitated in 24 h

Treatment of the filtrate by fractional vacuum distillation allows the recovering of a great amount of 3-CNT (cf I-2).

3-chloro-4-nitrostyrene (3-CNS) : a Wittig reaction was carried out by gradually adding sodium carbonate to a suspension of the phosphonium salt in a formaldehyde aqueous solution maintained at 35°C. The aqueous phase was surmonted by an organic solvent (e.g. cyclohexane) which extracts the most important part of the so formed styrene, thus isolates it from the alcaline solution and so avoids side reactions. Purification of the monomer was rather long because formaldehyde was carried along and fractional vacuum distillation had to be avoided because of an extensive loss of product due to thermal polymerisation. At room temperature 3-CNS is a liquid of very poor water solubility, but well miscible in all common organic solvents. Its structure was confirmed by ^{1}H NMR, ^{13}C NMR and 2D NMR spectroscopy.

II- Polymerization of 3-CNS :

These first attempts were intended to test the polymerisation ability of 3-CNS comparatively to its isomer 4-CNS. The question was to examine the real influence, in radical polymerization, of the nitro group position with respect to the vinyl group. Regardless on any classical effect, the highly electronwithdrawing nitro substituent in para position strongly polarizes the vinyl group by resonance and leads to a greater double bond reactivity. However the related radical is greatly stabilized by delocalisation resulting in its reactivity decrease which usually is the dominating effect.

Maximum of polymerization : attempts were carried out (Table 1) at relatively low temperature (51°C, in particular to minimize thermal polymerization) in the presence of a very active initiator in these conditions i.e 2,2'-azobis-(2,4-dimethylvaleronitrile) (ADVN).

In bulk polymerization, 3-CNS set to a mass after seven hours which never occured with 4-CNS with the same amount of initiator. This feature combined with 3 times higher conversion rates after 24h reaction and fairly high molecular weights, undoubtedly shows a much better ability of 3-CNS to polymerize compared to 4-CNS. These results can be well reproduced and one could interpret 4-CNS lower overall reactivity and even poor limiting conversions on the basis of the growing radical-double bond mutual reactivity. However, bulk polymerisation of 4-CNS in the presence of 0.88% (mole/monomer) of 2,2'-azobisisobutyronitrile at 65°C which, in these conditions, decomposes at the same rate than ADVN (calculated from data in toluene (18)) gave nearly the same conversion rate (17%). This lack of activation by temperature and systematic obtaining of rather low molecular weights even in other polymerisation conditions (4, 5) leads to suppose an unusual behaviour of 4-CNS.

Poly 3-CNS has very different solubility properties compared to poly 4-CNS, it is insoluble in aceton and chloroform and only sparingly soluble in THF which are solvents for the isomeric polymer. However, it is soluble in more polar solvents like DMF or DMSO.

Table 1. 3- and 4-CNS polymerization. Temp. : 51°C. ADVN initiator : 0.88% (mole/monomer). Size exclusion chromatography from solutions in 1-methyl-2-pyrolidone (0.75%).

Monomer	Method	Reaction time h	% yield	Molecular weight (SEC)
3-CNS	Bulk	24	53	7400 to 72800
3-CNS	50% in DMF	24	49	
4-CNS	Bulk	24	18	6900 to 16400
4-CNS	50% in DMF	24	20.5	

Polymerization kinetic : in order to evaluate, in a more accurate way, the difference of reactivity between the two monomers, a kinetic study of the bulk polymerization at 51°C was undertaken (Table 2) : conversion rates did not exceed 10% and reaction times were lower than 8h. With these limitations, the proportion of decomposed initiator remained low, propagation step was in the steady state assumption and volume contraction can be neglected.

Table 2. Bulk polymerisation of 3- and 4-CNS, conversion rate during time.Temp. : 51°C. Initiator ADVN 1% mole/monomer.

Reaction time min.	40	70	85	120	180	240	300
Yield %							
3-CNS	5.05	8.43	10.16				
4-CNS				2.5	3.97	5.43	6.53

The overall apparent polymerization rate can be written as :
$Rp = -d[M]/dt = d[P]/dt = k_1 [M]$ where [M] = monomer concentration, [P] = polymerized monomer units concentration. Concentrations [M] and [P] being proportional to the weight of formed polymer, the previous equation can be integrated as a function of the conversion rate i.e $X = w_t/w_f$, w_t = weight of polymer at time t, w_f = weight of polymer for a quantitative conversion and and the following expression is obtained $Y = -\ln(1-X) = k'_1 t$ (1)
Y values calculated from experimental data (Table 2) were plotted against reaction time for the two CNS isomers (fig.1). In the two cases, points are on straight lines which are going through origin. This corresponds to a first order kinetic with respect to monomer without induction time.
Slope of each straight line directly gives the value of the apparent first order rate constant k'_1 : retained values are these stemming from calculations taking into account the origin point. Results (t min) :
a) without (o,o) point :
4-CNS $Y = 2.36\ 10^{-4}t - 0.0024$ R = 0.998
3-CNS $Y = 12\ 10^{-4}t + 0.003$ R = 0.9999
b) with (0,0) point :
4-CNS $Y = 2.3\ 10^{-4}t - 0.00064$ R = 0.999
3-CNS $Y = 12.6\ 10^{-4}t + 0.0005$ R = 0.9999
Thus : 4-CNS $k'_1 = 2.3\ 10^{-4}$ min^{-1}
3-CNS $k'_1 = 1.26\ 10^{-3}$ min^{-1}

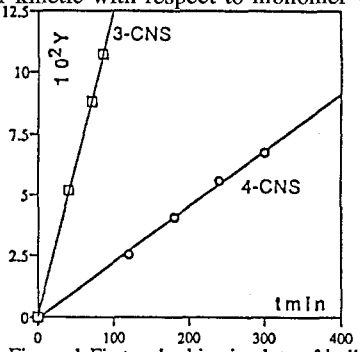


Figure 1 First order kinetic plots of bulk polymerization of 3- and 4-CNS. Temperature 51°C.Initiator ADVN 1%mol.

The overall reactivity of 3-CNS (i.e double bond and radical species) at the beginning of the reaction is therefore 5.5 times higher than the 4-CNS one. The low k'_1 value for 4-CNS could explain the poor conversion rate for long reaction times without futther addition of initiator because the calculated decomposition rate value of ADVN (k_d: 10^{-3} min^{-1}at 51°C in toluene, half life time : 10h from (18)) is 5 times higher than k'_1 and more in a polar medium like liquid 4-CNS. However this feature cannot be responsible for the significant decrease of molecular weight.

In the case of 3-CNS, whereas the growing radical is particularly stabilized by resonance due to the effect of the electronwithdrawing NO_2 substituent, the increase of overall reactivity is contradicting with what had been described concerning more usual monomers : styrene, dienes or acrylic monomers. However such an increase had been already observed in the case of para substituted (NO_2, CN, halogen) styrenes concerning propagation or copolymerization rate constants (11, 19) in comparison with styrene. This characteristic was ascribed to an exceptional affinity of the radical towards its monomer but every one of these reactivities could not be separately evaluated (18). Nevertheless one does not find

systematic studies on the influence of the substituent position and in particular, the case of meta substituted styrenes was not tackled. The above homopolymerisation results on two positional styrene isomers contribute to a first quantitative approach to this problem.

Conclusion

A new styrene monomer the 3-chloro-4-nitrostyrene (3-CNS) could be synthesized by a relatively short route. Its reactivity is markedly higher than 4-CNS isomers'one which results from the permutation of the two ring substituents. It makes it possible to achieve more easily the preparation of functionnal (cf introduction) polymers after chemical modification of the o-chloronitro site. The study also point out the importance of the position of an electronwithdrawing substituent, here NO_2, but the true role of such a group is yet not clearly understood. Other works based on copolymerization experiments or involving related monomers are under way to actually try to clarify that role as well as the halogen one.

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