Macromol. Symp. **2003**, *202*, 11–23

Novel Copolymers via Nitroxide Mediated Controlled Free Radical Polymerization of Vinyl Chloride

Thomas Wannemacher,[1] *Dietrich Braun,*[1,]* *Rudolf Pfaendner*[2]

[1] Deutsches Kunststoff-Institut, 64289 Darmstadt, Germany
[2] Ciba Spezialitätenchemie Lampertheim GmbH, 68623 Lampertheim, Germany

Summary: Controlled free radical polymerization (CFRP) of vinyl chloride (VCM) and copolymerization with several comonomers have been studied in aqueous suspension. Therefore di-tert-butylnitroxide and three novel nitroxyl radicals were used as mediating agents. Copolymerization of VCM with styrene, partly combined with acrylonitrile, maleic acid anhydride and maleic acid imide as well as methyl methacrylate, n-butyl methacrylate, butyl acrylate and butadiene have been achieved, demonstrating an efficient route for novel vinyl chloride copolymer architecture.

Keywords: block copolymers; CFRP; living polymerization; nitroxides; vinyl chloride

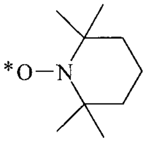
Introduction

In the last years living or controlled free radical polymerization (CFRP) processes have achieved a high level of industrial and academic interest. Besides Werrington and Tobolsky, who performed first attempts of controlling a radical polymerization reaction with specific disulfides in the mid fifties,[1] Otsu et al. introduced the IniFerTer-concept[2] as a true CFRP-concept thirty years later. First studies with nitroxide radicals or ethers were carried out and published in an US-Patent by Solomon[3] and coworkers. Finally atom transfer radical polymerization, ATRP[4] by Matyjaszewski and Sawamoto in 1995 and two years later Moad's RAFT-concept[5] (reversible addition fragmentation chain transfer) were introduced. Today the CFRP techniques are widely spread due to versatility with regard to monomers and functional groups, due to access to a wide range of processes and the possibility to build new polymer architectures.

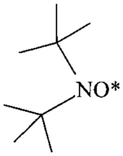
As PVC is one of the most important plastics with a number of applications, investigations of the polymerization of VCM in the presence of controlling agents and the synthesis of defined copolymers are of great interest. However, more than eighty percent of PVC is produced by suspension polymerization.[6] Therefore achievement of water based CFRP is a must.

DOI: 10.1002/masy.200351202

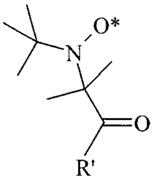
Due to the fact, that the ATRP technique is not applicable to some monomers such as vinyl chloride and RAFT is complicated in water based processes, other methods of controlling polymerization reactions are gaining relevance. Therefore, the nitroxide mediated CFRP shows many advantages in controlling the polymerization of different monomers and in building up new polymer architectures like block and graft copolymers which cannot be achieved by standard reaction methods.[7]



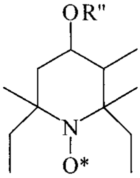
(1)



(2)



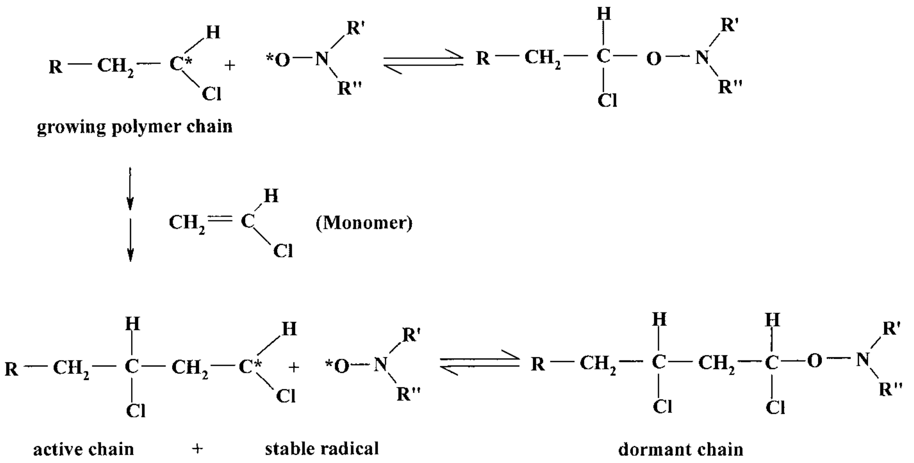
(3)



(4)

The well-known 2,2,6,6-teramethyl-piperidine-1-oxyl (TEMPO) (1), which is successfully used in CFRP processes with common monomers such as styrene,[8],[9] is not efficient in vinyl chloride polymerization. First, the VCM-polymerization temperature is at least about thirty degrees less than in styrene polymerization. Second, due to a certain water solubility TEMPO is not very attractive in suspension processes.[10] The novel, somewhat more sophisticated nitroxides used in this study are open chain structures, such as di-tert-butylnitroxide (2) with two symmetrical R's and a structure with different R's (3). Furthermore highly sterically hindered piperidine-like structures (4), comparable to TEMPO, have been investigated. These nitroxyl radicals have been selected due to their reduced water solubility and higher polymerization efficiency at lower temperature.

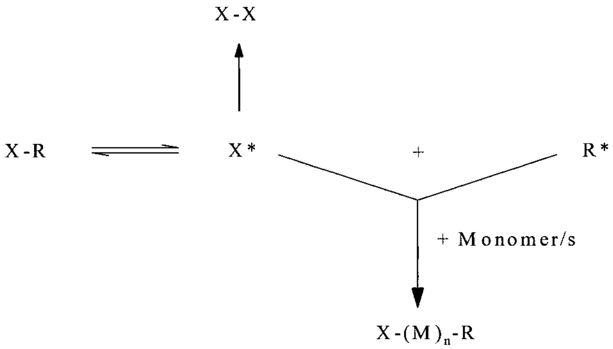
The main characteristic of the nitroxyl mediated polymerization is a thermal equilibrium as explained in scheme 1. At lower temperatures, the equilibrium is strongly shifted to the side with the attached nitroxide at the growing chain. The reversible termination of the growing chain is the key step for controlling the polymerization, resulting in a very low concentration of free radical chain ends. Due to this, irreversible termination reactions, such as chain-combination and disproportionation are minimized. Neglecting any side reaction, the polymer growth occurs in a living type manner with a high degree of control. After complete monomer consumption the polymer appears as a dormant chain with the nitroxide end group.



Scheme 1. Mechanism of nitroxide mediated controlled free radical polymerization.

A basic point of view is the so called persistent radical effect (PRE).[11] As shown in scheme 2 the initiator radical (X*) can undergo a reversible coupling with the nitroxide radical. A small amount of initiator radicals (transient radicals) irreversibly reacts with other radicals (initiator radicals or growing chain), which leads to a loss of initiator activity. By its nature, the mediating or persistent radical (the nitroxide) does not undergo any radical-radical coupling, so that a small amount of excess-radicals occurs. Therefore the ratio initiator : nitroxide plays an important role. The higher the concentration of excess free nitroxide, the higher is the amount of dormant chains. The reaction time increases, the polymerization rate and monomer conversion decreases. The overall results depend on temperature, monomer and the activity of the nitroxide.

Transient and persistent radicals are formed during the polymerization at the same extent, the persistent radicals do not interact with other persistent radicals but couple reversibly with transient radicals. The transient radicals, however, react among themselves irreversibly in self termination, the excess amount of persistent radicals grows in course of the reaction by simple stoechiometry. Because of this, the cross reaction gains on importance, the self terminating reactions are strongly inhibited, but never disappear completely.



Scheme 2. Description of the self-accelerating persistent radical effect (PRE).

Due to the fact that the polymerization of vinyl chloride bears some specific characteristics, the nitroxide mediated CFRP of VCM depends on the choice of the nitroxide compound. To our knowledge no literature data on nitroxide mediated CFRP of VCM have been published until now. Because of the chlorine, VCM has a very high resonance stability, and hence no cationic initiation is possible. Due to a high transfer constant, chain transfer reactions become very important. Molecular weight and polydispersity (PD) are mainly determined by the polymerization temperature. The lower the temperature, the higher the molecular weight, whereas reaction time, conversion, as well as concentration and type of the initiator have only a minor influence on the resulting polymer. Another point of view is, that with rising temperatures not only a decrease of the molecular weight appears, but a great reduction of the thermal stability of the polymer, which is undesirable.

Experimental Part

Materials

Vinyl chloride monomer (VCM) 3.7, 99,97 %, stabilized (supplier: Messer Griesheim) and butadiene 99,5 % (supplier: Linde) were used without purification. Styrene (supplier: BASF), methyl methacrylate (supplier: Röhm), n-butyl methacrylate (supplier: Röhm), butyl acrylate (supplier: BASF) and acrylonitrile (supplier: Fluka) were destabilized by shaking with NaOH solution or with a dehibit 200 column (polyscience inc.) and distilled under reduced pressure before use. Poly (vinyl alcohol) 7200, degree of hydrolysis 98 % (supplier: Merck) and citric acid (supplier: Merck) were used as suspending agents and maleic acid anhydride and maleic acid imide (supplier: Deutsche Texaco AG) as comonomers were used as received. 1,1-Dimethyl-2-ethylhexaneperoxoate (Luperox 26, supplier: Atofina) was used as initiator. All nitroxides were supplied by Ciba Spezialitätenchemie Lampertheim GmbH.

Homopolymerization of Vinyl Chloride Monomer

The polymerization was carried out according to the suspension process in batch operation. A double jacketed autoclave reactor (Buechi) of a volume of 500 ml was operated at a temperature between 70 °C and 90 °C with a stirrer velocity of 1000 rpm. The pressure amounts to 12-18 bar depending on the temperature used for the polymerization. Temperatures and pressure were recorded via pc during the reaction. Initiator concentration was 0.1 mole-% of acylic peroxide based on the vinyl chloride monomer. In order to avoid side reactions and to reduce undesired interactions with other compounds, the recipe was consciously reduced to the minimum of necessary substances. As suspending agent 0.3 g poly (vinyl alcohol) with a molecular weight of 40000, partly combined with a small amount of citric acid (15 mg) was used. The water : monomer ratio was 1 : 2.7, which is in the range of technical processes. Dosage of the VCM was accomplished by a Swagelock sample cylinder, connected with quick coupler. This also allowed a dosage of substances against the reactor pressure during the reaction. After a reaction time of 21 hours which was shown to be reasonable time for a monomer conversion of 50 % or more the obtained polymer was isolated by filtration resp. centrifugation. The crude polymer was washed with water, filtered, washed with ethanol, and finally dried under vacuum at 40 °C to constant weight.

Copolymer Formation Using Nitroxide Containing PVC as a Macroinitiator

Re-initiation experiments were carried out in a 100 ml Schlenk-tube. The solution consisting of PVC, monomer and solvent (chlorobenzene, 20 ml) was degassed and heated for 15 h or 21 h at the appropriate temperature under stirring. The mass ratio monomer : macroinitiator was 4 : 1; the ratio monomer/macroinitiator to solvent was 0.3. After cooling in an ice bath, the polymer was precipitated into 1500 ml methanol, filtered, washed with ethanol and dried under vacuum as indicated before.

Analytical Techniques

Molecular weights and polydispersities were determined in THF using a Waters modular GPC system equipped with 3 columns (PL, Polymer Laboratories 1×10^5, 2×10^4, 2×10^3 and 1×10^2 nm) thermostated at 30 °C and differential refractometer R401 (Waters) and UV detector at 254 nm (Waters). Calibration was done with narrow distributed polystyrene standards (supplied by Polymer Standard Service, PSS).

Thermal stability analysis was carried out according DIN 53 381, part 1. Therefore a small sample (100 mg) was filled in a pyrolysis vessel heated up to 180 °C in an oil bath. A pre-heated nitrogen stream (6 l/h) purged the developed HCl into a conductivity cell with demin. water (25 ml). The conductivity change was recorded with a Starna CDC1068 electrode and the HCl-conversion was calculated. As a measure of the thermal stability of the PVC samples the induction period $t_{ind.}$ is introduced as the section of the tangent of conductivity curve and the x-axis. Furthermore, stabilization time $t_{stab.}$ in our case is determined as the time when conductivity of the water in the sample cell reaches 50 µS cm^{-1} due to absorption of the evolved HCl in analogy to DIN 53 381, part 1, method B.

DSC investigations have been carried out with a differential scanning calorimeter DSC7 from Perkin Elmer under nitrogen atmosphere. Temperature range was from –200 °C to +110 °C with a heating and cooling rate of 20 °C min^{-1}. The sample weight was 10 mg.

Results and Discussion

Nitroxide Mediated Controlled Free Radical Polymerization of Vinyl Chloride Monomer

Nitroxide containing poly (vinyl chloride) was obtained via suspension polymerization process. The presence of the chemically bonded nitroxyl group in the PVC polymer could be proven indirectly by the reinitiation experiments described later. As expected, the resultant polymers revealed in all cases a narrower polydispersity (PD) than compared with S-PVC polymerized without nitroxide mediation (table 1-4). However, the polydispersities are not as low as in common CFRP processes with other monomers. This may be due to the occurrence of side reactions like disproportionation, which is a well-known fact in PVC manufacturing and has its cause in the very high transfer constant of the VCM ($C_M = 12 - 24 * 10^4$ at 70 °C). Nevertheless, high molecular weights are obtained even at elevated temperatures above 70 °C, which is very high for VCM polymerization. Variation of polymerization temperatures, nitroxide type and concentration has been investigated.

Table 1. Influence of the temperature on the molecular weight and the polydispersity.

	nitroxide	T (°C)	yield (%)	M_n (g mole^{-1})	M_w (g mole^{-1})	PD M_w/M_n	$t_{ind.}$ (min)	$t_{stab.}$ (min)
1	- [a)]	70	94	28000	51000	2.6	14	43
2	- [a)]	75	89	31000	72000	2.3	14	38
3	- [a)]	80	88	25000	58000	2.3	11	32
4	- [a)]	85	71	18000	47000	2.7	12	30
5	(2)	70	35	20000	41000	2.0	15	27
6	(2)	75	62	26000	56000	2.1	17	26
7	(2)	80	63	29000	56000	1.9	10	26
8	(2)	85	57	24000	50000	2.1	12	22
9	(2)	90	33	18000	38000	2.1	11	23

a) comparison experiments without nitroxide content
conditions: 0.1 mole-% Initiator, 0.05 mole-% nitroxide based on the vinyl chloride monomer, t=21h

As expected the addition of nitroxides leads to a reduction of the conversion rates. A narrower molecular weight distribution of the experiments with nitroxides indicates control of the polymerization. A direct influence on the thermal stability is not detectable in all cases except the experiments with TEMPO (cf. table 3), resulting in lower stability. However, as shown below TEMPO does not act as polymerization regulator (controlling agent) under the conditions of PVC polymerization.

Varying the nitroxide concentration (Table 2) also results in a variation of the initiator : nitroxide ratio which has a strong effect on the conversion. A decrease in its ratio corresponding to an increase in free nitroxyl leads to an increased reaction time and lower yield while the molecular weight and the thermal stability are not affected significantly.

Table 2. Influence of the nitroxide concentration at a polymerization temperature of 85 °C.

	nitroxide	concentration (mole-%)	yield (%)	M_n (g mole^{-1})	M_w (g mole^{-1})	PD M_w/M_n	$t_{ind.}$ (min)	$t_{stab.}$ (min)
10	-	-	76	19000	51000	2.7	11	30
11	(2)	0.025	56	20000	45000	2.2	15	28
12	(2)	0.030	65	20000	44000	2.2	9	19
13	(2)	0.050	42	19000	42000	2.3	9	19
14	(2)	0.075	38	17000	40000	2.3	10	20

conditions: 0.1 mole-% Initiator based on the vinyl chloride monomer, T=80 °C, t=21h.

Table 3. Influence of the nitroxide type.

	nitroxide	reaction time (h)	yield (%)	M_n (g mole^{-1})	M_w (g mole^{-1})	PD M_w/M_n	$t_{ind.}$ (min)	$t_{stab.}$ (min)
15	(1)	21	38	9000	22000	2.5	4.5	8
16	(2)	21	62	19000	46000	2.4	9	31
17	(3)	21	64	22000	51000	2.3	8	23
18	(4)	21	74	20000	46000	2.2	9	25

conditions: 0.1 mole-% Initiator, 0.05 mole-% nitroxide based on the vinyl chloride monomer, T=80 °C.

After 21h reaction time all different nitroxide types (with the exception of TEMPO) reveal higher molecular weights, lower polydispersities and much higher conversions, however lower than compared with the reaction without nitroxide addition. In all cases, the reaction time was prolonged up to 21 h. This is in contrast to conventional free radical suspension polymerization of VCM, where polymerization times of 4-7 h are usual. The highest conversion rate is achieved with a nitroxide concentration of 0.03 mole-%. For achieving control in PVC polymerization the use of nitroxyl structures with high steric hinderance is essential.

As clearly seen in Table 3, TEMPO (1) reduces conversion and molecular weight in contrast to other nitroxide types. As depicted before, TEMPO is not efficient for CFRP-processes at temperatures below 100 °C. Also TEMPO mediated PVC shows a relatively low thermal stability. This may be interpreted as an increase of side reactions leading to non-ideal (linear) PVC chain structures.

Random Copolymerization of VCM and Vinyl Acetate

As one of the most popular comonomer for VCM, vinyl acetate (9) is largely used in technical copolymerizations. Therefore it was obvious to use this comonomer in the CFRP process. The copolymerization reactivity rates of vinyl chloride / vinyl acetate are $r_1 = 1.68$ and $r_2 = 0.23$[12] at 68 °C, which implies that vinyl chloride preferentially polymerizes compared to the vinyl acetate. As a consequence, in normal radical polymerizations the initially formed copolymer is lower in vinyl acetate content relative to the comonomer composition. This ratio shifts during the copolymerization towards an increasing content of vinyl acetate. Due to the very low concentration of free radicals and the fact, that all chains are growing approximately with the same rate, the copolymers have a constant composition during the entire polymerization process. This has been shown by Hawker et al.[13] with the copolymerization of styrene/maleic acid anhydride mixtures.

In our experiments VCM / vinyl acetate random copolymers with a vinyl acetate content of 10-50 % (w/w) have been successfully obtained in suspension in the same way as described for the homopolymerization (Table 4).

Table 4. Conditions and results of random copolymerization of VCM and vinyl acetate.

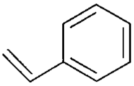
	VCM	vinyl acetate	T (°C)	yield (%)	M_n (g mole^{-1})	M_w (g mole^{-1})	PD M_w/M_n
19	0.5	0.5	85	64	22000	49000	2.2
20	0.85	0.15	72	92	18000	42000	2.3
21[a)]	0.9	0.1	72	60	27000	57000	2.1
22	0.9	0.1	80	67	27000	54000	1.9

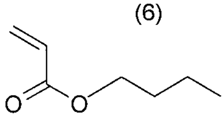
conditions: 0.1 mole-% Initiator, 0.05 mole-% nitroxide (2) based on monomers; t=21 h
a) t=45 h

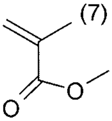
The experiments with a high content of vinyl acetate mostly showed a coagulation of the suspension, but with a content of 10 % comonomer similar molecular weights compared to the pure PVC polymerization were obtained. At the temperature of 80 °C high molecular weight and the narrowest molecular weight distribution were reached. The copolymer composition and its regularity are still under investigation. Samples with a higher content of vinyl acetate revealed a strong coloring towards brown. This discoloration disappeared after re-precipitating.

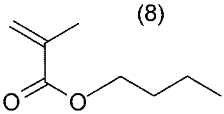
Re-initiation Experiments

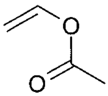
To demonstrate the capability of reinitiation and formation of block copolymers from the PVC obtained via nitroxyl mediated polymerization, these nitroxide containing dormant chains were re-awakened by heating up in the presence of a second monomer.

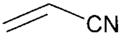

(5)

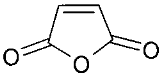

(6)

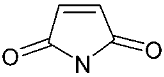

(7)

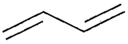

(8)


(9)


(10)


(11)


(12)


(13)

We investigated a number of common monomers such as styrene (5), butyl acrylate (6), methyl methacrylate (7) and butyl methacrylate (8), acrylonitrile (10), MAA (11), MAI (12) (in combination with styrene) and even butadiene (13) in terms of the possibility of re-initiation.

At temperatures of 100 – 130 °C, the nitroxyl containing PVC acts as a macro-initiator and starts a new polymerization reaction. Due to this elevated temperatures, the controlled reaction should proceed without any problem especially with monomers like styrene, which are known to undergo very easily the nitroxide mediated CFRP. The resulting polymer is an A-B-type two-block copolymer as proved by GPC measurements (cf. Fig. 1). The incorporation of styrene can be shown by an increase in molecular weight and by uv-activity of the sample.

Addition of campher sulphonic acid (CSA) (examples 27, 28) accelerates the polymerization rate as known from[14] and prevents the auto-initiation of styrene, which is a significant reaction at the chosen polymerization temperatures. With reference experiments it could be shown, that the auto-initiation process is largely suppressed. Furthermore the addition of stearyl-benzoyl-methane as a well-known thermostabilizer for PVC[15] to the reaction solution (example 29 and 30) results in reduced discoloration of the sample according to improved thermal stability of the PVC polymer resulting in a pure colorless block copolymer.

Table 5. Results of the re-initiation experiments.

	second / third monomer (+ optionally additive)	temp (° C)	yield[a)] (%)	M_n (g mole^{-1})	M_w (g mole^{-1})	PD M_w/M_n
23	NO*-containing pure PVC (13)	130	91 [b)]	20000	36000	1.8
24	styrene	100	30	17000	53000	3.5
25	butyl methacrylate	130	41	24000	60000	2.5
26	styrene + acrylonitrile (1:3)	110	15	24000	72000	3.0
27	styrene + MAA (1:1) + CSA 10 mg	130	98	Not determined		
28	styrene + MAI (1:1) + CSA 10 mg	130	68	30000	79000	2.7
29	methyl methacrylate + Stab 10 mg	130	54	29000	86000	3.0
30	butyl acrylate + Stab 10 mg	120	22	19000	39000	2.0

a) yield: conversion 2nd monomer
b) recovery of the original PVC
CSA = campher-10-sulfonic acid, MAA = maleic acid anhydride, MAI = Maleic acid imide, Stab = Stearyl-benzoyl-methane.

The successful reactivation reaction can be proved by GPC (Figure 1). There is no transfer to a new starting polymer chain of the second monomer. The initial nitroxide-containing PVC shows no UV-activity. After the re-initiation reaction, first an UV-absorption due to the aromatic styrene function can be seen. But there is also a shift to higher molecular weight and no second signal at the position of the initial PVC or any signal from other polymerization products is detected.

Furthermore butadiene (13) was used as second monomer. This monomer was easily dosed into the reactor after complete consumption of the VCM without purifying the original PVC. The reactor just was degassed and filled with gaseous butadiene monomer in the same manner as described for VCM. While butadiene is known as a good inhibitor of the VCM polymerization it can be proposed, that also an AB-type copolymer is resulting; however it was not confirmed by any analytical technique. The obtained polymer with the overall conversion of 13% shows a molecular weight of 39000 (M_w) and a polydispersity of 2.0. This material exhibits the expected rubber-like appearance and a soft touch contrary to the rigid hard PVC. Indication of copolymer formation is shown by DSC and by appearance of a mixed glass transition temperature T_g at 22 °C in addition to the typical T_g of polybutadiene at – 86 °C and PVC at + 87 °C. A complete analytical investigation in terms of copolymer composition and block structure will follow.[16]

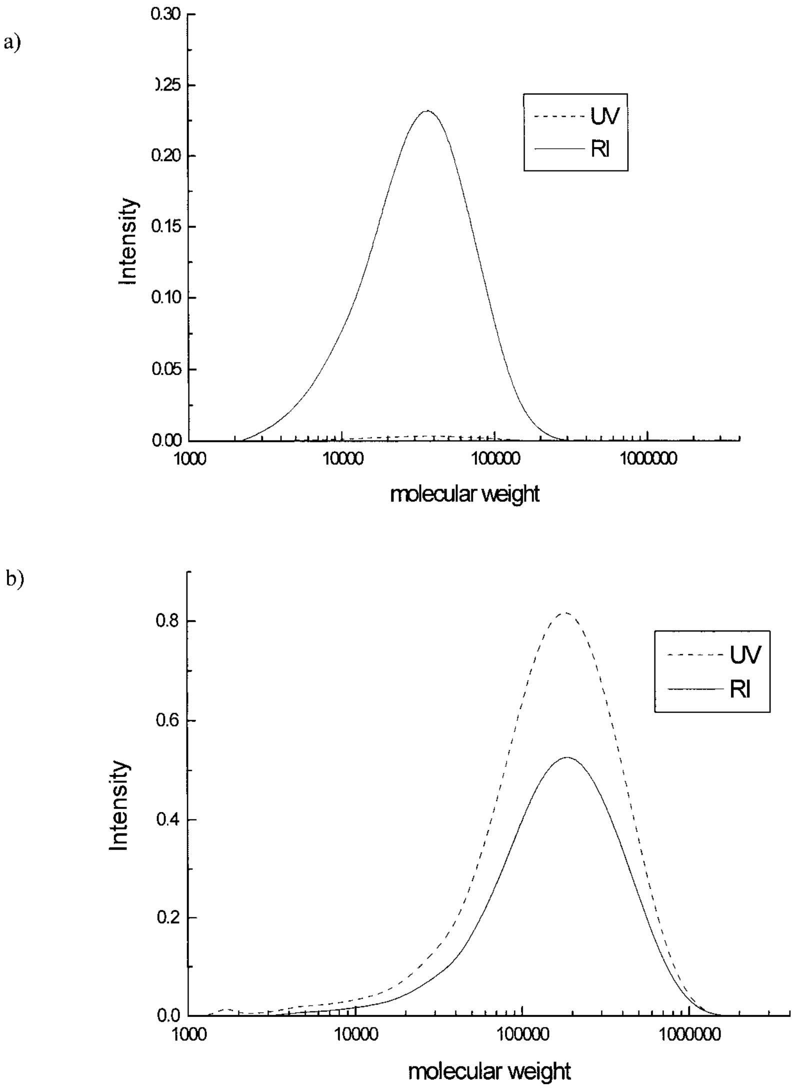


Fig. 1. a) Pure PVC polymerized in the presence of (4) is not absorbing in UV (only RI = Refractive Index).
b) Re-initiation of the PVC with styrene results in intense UV-absorption due to incorporated polystyrene and at the same time increase in molecular weight.

Conclusion

Nitroxide-mediated CFRP of vinyl chloride monomer was performed in suspension process, leading to PVC-homopolymers with a narrower molecular weight distribution. Contrary to classical PVC polymerization the molecular weight can be kept high at higher polymerization temperatures. The resulting nitroxide-containing PVC acts as a macroinitiator and forms different types of copolymers. Random copolymers of VCM with vinyl acetate, AB-type two-block copolymers with styrene, methyl methacrylate, n-butyl methacrylate, n-butyl acrylate and butadiene and terpolymers with one PVC block and two monomer(s) (styrene/methyl methacrylate, styrene/acrylonitrile, styrene/maleic acid anhydride and styrene/maleic acid imide) in the second block have been synthesized. Therefore, the living-type nitroxyl mediated polymerization of VCM opens new ways for the design of complex polymer architectures on the basis of PVC structures.

Acknowledgements

Ciba Spezialitätenchemie Lampertheim GmbH, Lampertheim, Germany is gratefully acknowledged for financial support, and for providing the nitroxide samples.

[1] T.E. Werrington, A.V. Tobolsky, *J.Am.Chem.Soc.* **1955**, *77*, 4510

[2] T. Otsu, M. Yoshida, *Makromole.Chem. Rapid Commun.* **1982**, *3*, 124

[3] D.H. Solomon, E. Rizzardo, P. Cacioli, *U.S. Patent 4,581,429*, **1986**

[4] a) J.-S. Wang, K. Matyjaszewski, *J.Am.Chem.Soc.* **1995**, *117* 5614; b) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules*, **1995**, *28*, 1721

[5] J. Chiefari, Y.K. Chong, F. Ercole, J. Krstina, J. Jeffery, T.P.T. Le, R.T.A. Mayadunna, G.F. Meijs, C.L. Moad, G. Moad, E. Rizzardo, S.H. Thang, *Macromolecules* **1998**, *31*, 5559

[6] Verband Kunststofferzeugende Industrie **2002**

[7] C.J. Hawker, A.W. Bosman, E. Harth, *Chem.Rev.* **2001**, *101*, 3661

[8] M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, *Macromolecules* **1993**, *26*, 2987

[9] M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, *Trends Polym. Sci.* **1993**, *2*, 66

[10] C.J. Hawker, G.G. Barclay, A. Orellana, J. Dao, W. Devonport, *Macromolecules* **1996**, *29*, 5245

[11] a) H. Fischer, *Macromolecules* **1997**, *30*, 5666 b) H. Fischer, *Chem.Rev.* **2001**, *101*, 3581

[12] F.R. Mayo, C.Walling, F.M. Lewis, W.F. Halse, *J.Am.Chem.Soc.* **1948**, *70*, 1523

[13] D. Benoit, C.J. Hawker, E.E. Huang, Z. Lin, T.P. Russell, *Macromolecules* **2000**, *16*, 2143

[14] P. G. Odell, P. N. Veregin, G. K. Hamer, M. K.Georges, *U.S. Patent 5,608,023*, **1995**

[15] A. Michel, T.V. Hoang, B. Perrin, M.F. Llauro, *Polym.Degrad.Stab.* **1980**, *3*, 107

[16] T.Wannemacher, Dissertation, in press

[17] T.Wannemacher, Dissertation, in press