Investigation of Polymer Miscibility by Spectroscopic Methods. III. Labeling of Poly (Vinyl Chloride), Poly(Methyl Methacrylate) and Poly(styrene-co-acrylonitrile) with Fluorescent Chromophores for Nonradiative Energy Transfer Studies

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Synopsis

Poly(vinyl chloride) (PVC) is generally recognized as miscible with s.poly(methyl methacrylate) (s.PMMA), poly(ϵ-caprolactone) (PCL) and poly(styrene-co-acrylonitrile) copolymer (SAN) containing 27 wt % AN. Nonradiative energy transfer (NRET) is a very sensitive technique in the investigation of the polymer miscibility. To compare by NRET the actual degree of miscibility of the PVC/s.PMMA, PVC/PCL, and PVC/SAN polymer pairs, each polymer is to be labeled with a fluorescent chromophore to an extent of 1 or 2 mol %. This paper reports efficient pathways to attach anthracene (acceptor) or naphthalene (donor) onto preformed PVC, s.PMMA, and SAN samples. All the attempts for grafting carbazole (donor) moieties have failed, as well as any labeling of PCL whatever the nature of the chromophore.

INTRODUCTION

Polymer blends are presently a focus of great interest in the development of new organic materials, and assessing the compatibility of polymer pairs or the phase state of their mixtures is of prime importance in this connection.[1] The methods most frequently used for compatibility studies are measurements of glass transition by calorimetry and dynamic mechanical testing.[1] According to Kaplan, a minimum segmental length of 15 nm should however be required to detect the glass transition of a polymeric component.[2] Electron microscopy is another investigation technique with a higher power of resolution, but insufficient electronic contrast between polymeric partners as well as artifacts in the observation of very thin films are often mentioned limitations.[3] Therefore, new and highly sensitive techniques are required to obtain experimental evidence for the presence of either molecular dispersion or very finely dispersed phases. Pulsed NMR can contribute efficiently to the resolution of this problem.[4-7] Inverse gas chromatography and neutron scattering are methods of recent application, suitable to quan-

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tify the thermodynamic interactions between segments of different polymers.[8,9] Nonradiative energy transfer (NRET), a well-known method to characterize intramolecular distances in biological macromolecules,[10] has recently been extended by Morawetz to the study of polymer compatibility.[11–15] The most striking characteristic of NRET is its ability to characterize a continuous modification of the interpenetration of polymeric components, rather than make the merely qualitative distinction between "compatible" and "incompatible" systems. In this technique, the energy transfer between two polymeric species labeled with donor and acceptor chromophores, respectively, is a very sensitive indicator of polymer compatibility. The emission spectrum of the donor has to overlap the absorption spectrum of the acceptor so that the energy absorbed by the donor is transferred by a nonradiative process to the acceptor over distances of the order of 2 nm. As a consequence, energy transfer is favored by the mutual interpenetration of polymeric species and vice-versa.

Since studies on polymer blends often have to deal with preformed block copolymers or commercially available polymers, this paper will describe direct labeling methods allowing the investigation of their compatibility by NRET. In his pioneering work, Morawetz performed the labeling by copolymerization with monomers carrying the desired label, except for materials containing anionically polymerized styrene or α-methylstyrene to which the labels were attached after a light chloromethylation.[13,15] As far as compatible polymer pairs are concerned, attention is often paid to poly(vinyl chloride) (PVC) because of its apparent miscibility with various polymers, like syndiotactic poly(methyl methacrylate) (s.PMMA), poly(ϵ-caprolactone) (PCL), and random styrene–acrylonitrile copolymer (SAN).[1] NRET appears as an efficient method to compare the actual degree of miscibility of PVC with s.PMMA, PCL, and SAN. It is the reason why we have been concerned with the labeling of the mentioned polymers with fluorescent chromophores and more specifically, anthracene (acceptor) and naphthalene or carbazole (donors). This paper reports the chemical pathways tested in that respect.

EXPERIMENTAL

Polymers

Poly(vinyl chloride) (PVC) and a styrene/acrylonitrile copolymer (SAN) containing 27 wt % AN were commercial products kindly supplied by Solvay (PVC RD 258) and Labofina (SAN K11), respectively. They were purified by a twofold precipitation from THF into methanol, in order to remove any stabilizer and plasticizer residue. The polymers were dried under reduced pressure up to constant weight, and PVC was kept in the darkness. Poly(methyl methacrylate) (PMMA) was prepared by anionic polymerization initiated by diphenylmethyl lithium in THF, at −78°C, under the usual conditions of dryness and inert atmosphere. It contained 89% of syndiotactic triads and 11% of heterotactic ones, as determined by ^{1}H NMR (Cameca 250 MHz) in *o*-dichlorobenzene solution (5 wt % PMMA) at 130°C.[16] Poly (ϵ-caprolactone) (PCL) was synthesized in toluene with Al isopropoxide as

catalyst; experimental details have been reported elsewhere.[17] Poly(styrene-b-MMA) was obtained by sequential anionic polymerization initiated by *sec*-butyllithium, in THF, at −78°C; styrene was of course polymerized first. MMA was dried over triethylaluminum and styrene over calcium hydride. Table I summarizes the main molecular features of the polymers used in this investigation.

Labeling of Polymers

9-methylanthryl lithium (I) and α-methylnaphthyl lithium (II) used in the labeling of PVC and PMMA were prepared by metalation of 1,2-di(9-anthryl) ethane (III) and 1,2-di(αα'naphthyl)ethane (IV), respectively. III was prepared from 9-anthraldehyde (V) according to the method reported by Schreiber and Emerson,[18] whereas V was synthesized as previously described.[19] IV was obtained by the procedure of Copeland et al.[20] The average yield of the synthesis of III, IV, and V ranged from 50–60%. The metalation of III and IV was performed in carefully dried THF, using only a slight excess of bright metallic lithium. The reaction was started at −78°C and once the ion-radical had formed (change in color), the temperature was allowed to increase up to 25°C. When the reaction seemed to reach completion (i.e., I was deep green and II was deep red), the solution was separated from the unreacted lithium to prevent any further reduction.[21] The organolithium concentration (0.03-0.05 $m.l^{-1}$) was determined by the Gilman's double titration[22] and the yield of the metalation process was about 70%.

I or II was then added dropwise into a dry solution of PVC in THF (1 wt %), at 0°C, under a nitrogen atmosphere. The labeled PVC was purified by a twofold precipitation from THF into methanol followed by a twofold precipitation from THF into hexane, to remove the unattached chromophores and impurities like grease residue. UV measurements were used to ascertain the efficiency of the purification procedure; at this stage, the molar percentage of chromophore attached onto PVC remained constant upon further purification. 9-methylanthracene and α-methylnaphthalene were used as standards to determine the concentration of each chromophore.

The labeling of PMMA was performed by adding a solution of I into dry THF containing PMMA (1 wt %), at 25°C, under nitrogen. The recovery and purification of the labeled PMMA were achieved in the same way as the labeled PVC. SAN was labeled in highly dilute solution (1 wt %) in THF, at −78°C, by adding successively equimolar amounts of dried 9-chloromethylanthracene and lithium diisopropylamide, both in THF solution.

TABLE I
Molecular Features of the Available Polymers[a]

Polymer	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
PVC	43,000	80,000	1.86
PMMA	150,000	190,000	1.27
SAN	54,000	130,000	2.41
PCL	22,000	36,000	1.64

[a] As determined by GPC in THF at 25°C.

After 1 or 2 h, the reaction was stopped by the addition of a dilute hydrochloric acid solution. The polymer was recovered, purified and characterized as before. The lithium diisopropylamide **VI** was prepared by reacting equimolar amounts of *n*-BuLi and diisopropylamine previously dried over molecular sieve. The reaction proceeded in dry THF, at −78°C, for 10–15 min.; the solution of **VI** was prepared just before use.

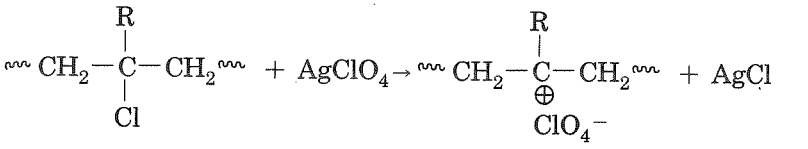
All of the labeled polymers were carefully kept in the dark. THF was dried by refluxing over the benzophenone–Na complex under nitrogen and distilled just before use. Polymers and solid reagents were dried by azeotropic distillation of THF. More precisely, a flask containing a THF solution of the material to be dried was connected to another one containing poly(styryllithium) (PSLi). Under reduced pressure, THF was distilled over PSLi which reacted immediately with any protic compound. The THF distillation was reversed and the cycle was repeated as much as necessary. GPC was performed on a Waters 200 apparatus operating in THF at 25°C. UV visible spectra were recorded with a Varian Techtron spectrophotometer, model 635.

RESULTS AND DISCUSSION

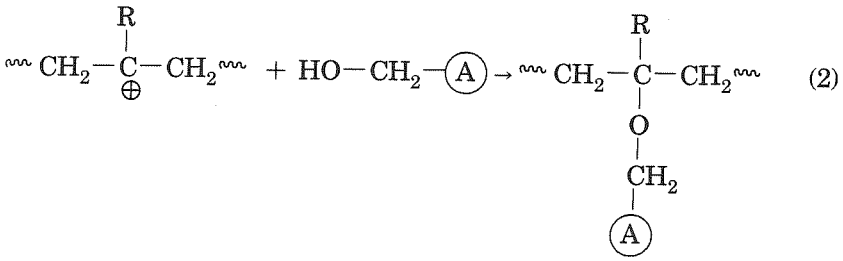
Carbazole–anthracene and naphthalene–anthracene are quite suitable pairs of fluorescent chromophores.[12] To prevent the labels to modify the intrinsic miscibility of polymers, the labeling should be limited to the lowest percentages of chromophores possible. In that respect, remember that Morawetz generally prepared labeled polymers carrying ca. 1–2 mol % fluorescent residues. Labeled polymers were then diluted with the similar unlabeled one so as to achieve a $10^{-2}M$ concentration in donor and acceptor in the blends, whatever their composition.[13] These chromophores should also be attached onto the polymeric backbone in such a way that their spectral features remain unmodified. So, a chromophore of low molecular weight can be used to build up a calibration curve suitable for determining the concentration of the attached chromophores from the Beer–Lambert law. Furthermore, the spectroscopic features of model chromophores are generally tabulated[23] and these data are useful to anticipate the way in which the NRET will proceed. Finally, a blend consisting of donor- and acceptor-labeled PVC chains can be referred as to the required state of ideal miscibility: reaction pathways should therefore be devised to attach both the donor and the acceptor chromophores onto one same polymer, e.g., PVC.

Labeling of PVC

A SN_1 nucleophilic substitution was first considered in order to attach a chromophore onto PVC. Due to structural defects, a few tertiary chlorine atoms are indeed present,[24] and may give rise to carbocations in the presence of silver salts.[25] The cations can then react with, e.g., 9-anthrylmethanol according to a SN_1 substitution:



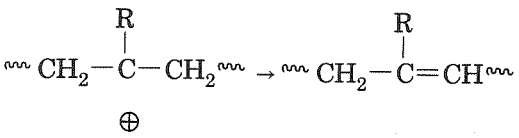
(1)



(2)

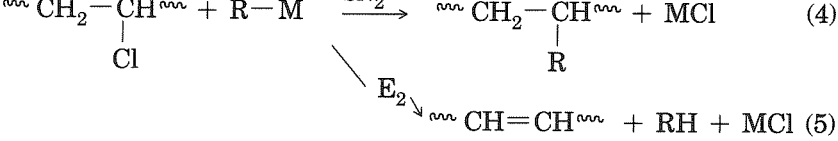
with A used for the anthracene residue.

Unfortunately, an E_1 elimination reaction was mainly observed:



(3)

On the other hand, a nucleophilic reagent carrying a chromophore unit (anthracene or Ⓐ, naphthalene or Ⓝ, and carbazole or Ⓒ) is able to promote the SN_2 nucleophilic substitution of the secondary chlorine atoms of PVC, resulting in the attachment of the chromophore onto the polymeric backbone. The previously reported synthesis of poly(vinyl chloride-g-styrene) or poly(vinyl chloride-g-butadiene) is based on that reaction scheme.[26,27] Nevertheless, an E_2 elimination can compete with the SN_2 mechanism producing the formation of conjugated double bonds in PVC. These two possible pathways are schematized by:



(4)

(5)

where RM is a nucleophile reagent comprising the chromophore residue (R) and an alkaline metal (M).

The SN_2 mechanism is known to be favored when the reagent's nucleophilicity prevails over its basicity. The reaction should be therefore performed at low temperature (−78°C), using the smaller Li gegenion.

The use of a lithium alcoholate, e.g., 9-anthryl Li methanolate, gave disappointing results. The anchoring of the chromophore was not observed whereas the elimination reaction was responsible for the formation of conjugated double bonds, as shown by the UV visible spectrum of the so mod-

ified PVC (Fig. 1).[28,29] The insufficient reactivity and the basic rather than nucleophilic character of the alcoholate could explain the failure of the expected substitution reaction. This hypothesis was assessed by the efficiency of carbanions in labeling PVC. Indeed, when a dilute solution of 9-methylanthryl Li or α-methylnaphthyl Li in THF was reacted with PVC (1 wt %), at 0°C, no meaningful degradation of PVC occurs whereas the chromophore was successfully attached onto the polymer.

Figures 2 and 3 report the UV–visible spectrum of the anthracene- and naphthalene-labeled PVC, respectively. It is very difficult to observe the characteristic absorption of polyenes, especially from Fig. 2 wherein the very strong absorption of anthracene below 250 nm can cover the absorption due to very short polyene sequences. Nevertheless, the slightly higher absorption of the anthracene-labeled PVC at 335 nm (Fig. 2) compared to that of 9-methylanthracene (Fig 4) could be indicative of the formation of a few conjugated double bonds. The recovered PVC is however colorless. The characteristic absorption of anthracene and naphthalene residues is unambiguously observed (Figs. 2 and 3) and assessed by reference to the spectrum of 9-methylanthracene (Fig. 4) and α-methylnaphthalene (Fig. 5) used as respective model compounds. A small but constant shift of 2 nm is however reported in the absorption maxima of the model and the attached chromophores; this is probably due to the vicinity of the chlorine atoms of PVC. About 50% of the organolithium compounds participate to the labeling which means that part of them is killed by impurities and/or involved in secondary reactions such as a metal-halogen exchange process. If efficient, this latter reaction should be responsible for chain coupling with formation of branched and ultimately cross-linked polymer. PVC remained however quite soluble, but the initial molecular weight distribution, as observed by GPC, was slightly shifted towards higher molecular weights (Fig. 6). At all events, the relative importance of potential secondary reactions remains

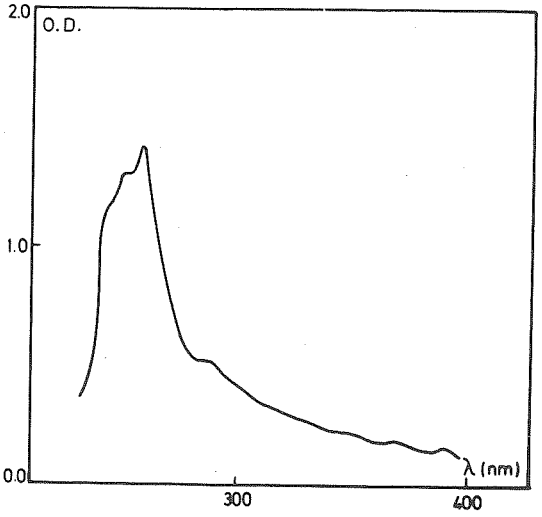


Fig. 1. UV–visible spectrum of PVC recovered after reaction with 9-anthryl Li methanolate.

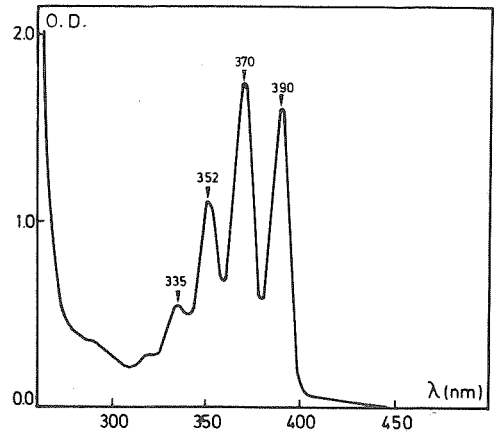


Fig. 2. UV–visible spectrum of 9-methylanthryl labeled PVC.

quite limited due to the high dilution of the reaction medium (1 wt % PVC) and the low amount of labeling required (i.e., 1–2 mol % of vinyl chloride units).

It is noteworthy that the synthesis of a chromophore containing Li carbanions, through the classical metallation reaction of halogeno compounds:

$$RX + 2Li \rightarrow RLi + LiX \tag{6}$$

where R is the 9-methylanthryl and α-methyl naphthyl residue, respectively, gave very poor results. Another efficient pathway may however be found in the metallation by lithium of 1.2-di(9-anthryl)ethane[30] and 1,2-di (αα′naphthyl) ethane,[31] respectively. In that way, 70% yields could be obtained.

$$R—CH_2—CH_2—R + 2Li \rightarrow 2R—CH_2\,Li \tag{7}$$

where R is the anthryl or naphthyl moiety, respectively. The labeling of

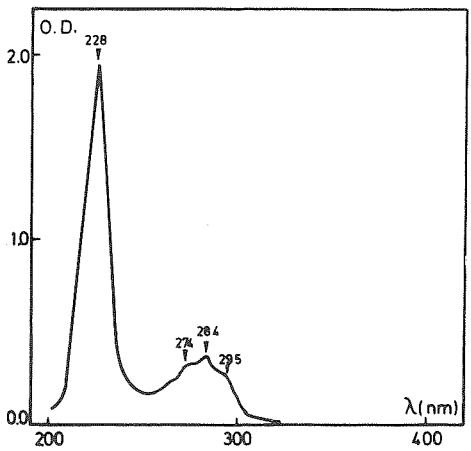


Fig. 3. UV–visible spectrum of α-methylnaphthyl-labeled PVC.

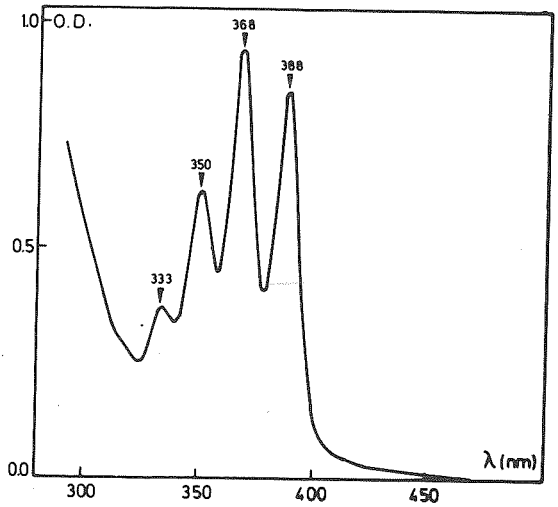


Fig. 4. UV-visible spectrum of 9-methylanthracene.

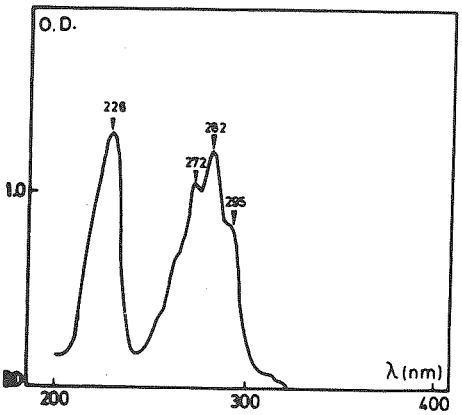


Fig. 5. UV–visible spectrum of α-methylnaphthalene.

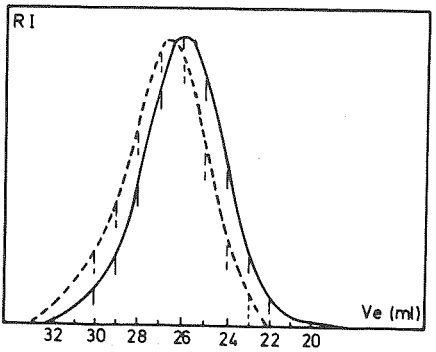
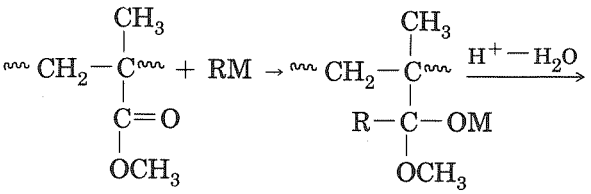


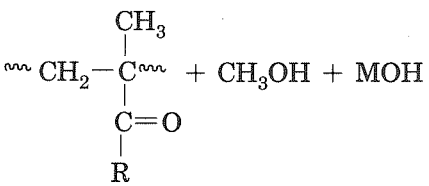
Fig. 6. Gel permeation chromatography of PVC, (- - -) before and (—) after labeling with 9-methylanthryl lithium.

PVC with carbazole residues has not been attempted because no suitable organolithium derivative was available. Furthermore the known halogenoalkylcarbazoles (Ⓒ– $(CH_2)_n$–X, with $n \geqslant 2$)[32,33] can only promote the synthesis of an aliphatic type organolithium which usually favors the elimination rather than the substitution reaction.

Labeling of PMMA

Nucleophiles, such as organomagnesium or organo alkali metal derivatives carrying fluorescent chromophores (RM), could be quite suitable for labeling PMMA through addition reaction onto the carbonyl of the ester groups:



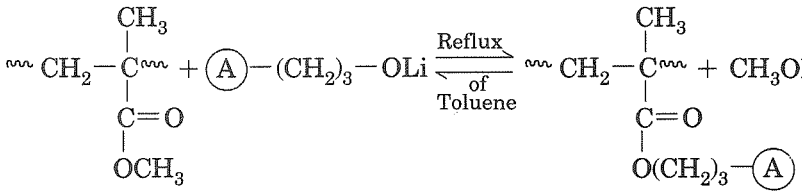


(8)

This reaction pathway was thus considered in order to attach carbazole onto PMMA. In that respect, 2-(*N*-carbazolyl) ethyl magnesium bromide and *N*-carbazolyl sodium were synthesized and used as nucleophiles. 2-(*N*-carbazolyl) ethyl bromide is easily prepared from carbazole and a large excess of 1,2-dibromoethane through a phase transfer reaction;[34,35] the derived organomagnesian is obtained in a 80% yield. *N*-carbazolyl Na results from the reaction of carbazole with sodium hydride.[33] The addition of the so prepared nucleophiles onto PMMA has proved to be a poorly efficient labeling method. The UV–visible spectrum of the recovered and purified PMMA does indeed show only traces of attached fluorescent labels. It is assumed that the steric hindrance of the carbazole residue could at least partly explain these disappointing results. It is also meaningful that a less crowded organomagnesian, such as 4-phenyl *n*-butyl magnesium bromide, was efficiently attached onto PMMA under the same reaction conditions. Besides that problem of steric hindrance, an insufficient reactivity of the used nucleophiles could at the same time be responsible for poor labeling yields. Because of difficulties in the synthesis of 2-(*N*-carbazolyl) ethyl lithium through the classical metallation pathway, 9-methyl-anthryl lithium and α-methylnaphthyl lithium were used as more reactive organometallic compounds. The addition reaction [eq. (8)] proceeds now quite satisfactorily

when the reaction temperature increases slowly from 0°C up to 25°C (50% yield), and PMMA is not affected by any degradation mechanism. The UV–visible spectrum of anthracene- and naphthalene-labeled PMMA is exactly the same as that of the corresponding low molecular weight analogue of the fluorescing residue, i.e., 9-methylanthracene and α-methyl-naphthalene, respectively. The same procedure could be used to label successfully the PMMA block of poly(styrene-b-methylmethacrylate).

For the sake of completeness, a transesterification approach was also tested as a labeling pathway of PMMA:

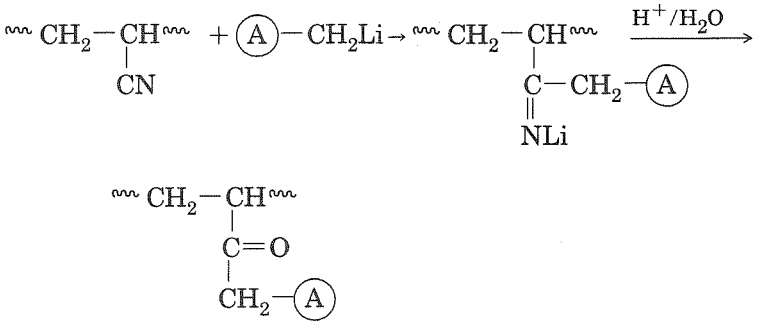


(9)

3-(9-anthryl) Li n.propanolate was prepared by reaction of ethylene oxide with 9-anthryl methyl lithium. As only 1 or 2 mol % of the ester groups are to be modified, a defect of lithium alcoholate with respect to the stoichiometry in eq. (9) was used, and could partly explain the unsatisfactory final results.

Labeling of SAN

The reaction of organolithium compounds with nitriles followed by hydrolysis is a well-known method for synthesizing ketones. When applied to random copolymers of styrene and acrylonitrile (27 wt % AN) this reaction resulted in the attachment of anthryl residues from 9-anthryl methyl lithium:



(10)

Unfortunately, a secondary reaction, the mechanism of which is not yet well understood, was responsible for an extensive degradation of SAN as shown by the gel permeation chromatography of the recovered copolymer (Fig. 7).

In a different approach, the hydrogen atom in α-position with respect to the nitrile can be removed by a base with formation of a carbanion. In the presence of an alkyl halide, an alkylation process may occur.[36] *N*-lithium diisopropylamide is a suitable base, the bulkiness of which prevents further attack of the nitrile group, whereas 9-anthrylmethyl chloride or α-na-

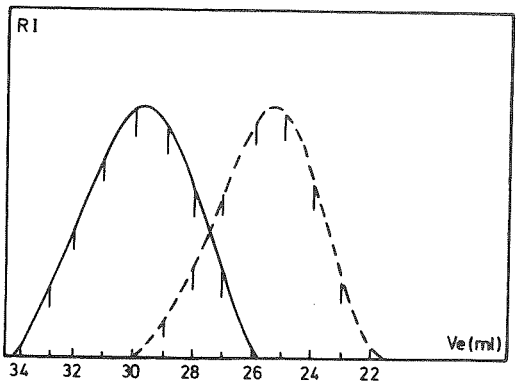


Fig. 7. Gel permeation chromatography of SAN, (- - -) before and (—) after labeling with 9-methylanthryl lithium.

phthylmethyl chloride are appropriate alkylating agents:

$$[(CH_3)_2CH]_2NLi + \sim CH_2-\underset{\underset{CN}{|}}{CH}\sim \rightarrow \sim CH_2-\overset{\overset{\ominus Li^+}{|}}{\underset{\underset{CN}{|}}{C}}\sim$$

$$+ [(CH_3)_2CH]_2NH \qquad (11)$$

$$\sim CH_2-\overset{\overset{\ominus Li^+}{|}}{\underset{\underset{CN}{|}}{C}}\sim + \textcircled{A}-CH_2Cl \longrightarrow \sim CH_2-\overset{\overset{CN}{|}}{\underset{\underset{CH_2-\textcircled{A}}{|}}{C}}\sim + LiCl \qquad (12)$$

A detailed study of this labeling process concluded to the successful anchoring of anthracene (or naphthalene) onto SAN (reaction yield > 50%) but also to the polymer degradation. By adjusting carefully the experimental conditions, it was however possible to limit the extent of this degradation reaction. In that respect, the alkylating agent should be added into the reaction medium before or just after lithium diisopropylamide, and the reaction should advantageously take place at low temperature (−78°C). Aiming at the alkylation of only 3 mol % of the nitrile units in a highly dilute solution (1 wt % of SAN) is in favor of the alkylation rather than the degradation of SAN. Independently of the degradation process, another secondary reaction occurred as revealed by the UV visible spectrum of the labeled polymer.

Figure 8, wherein by comparison with Figure 4 the relative absorption at 388 nm is increased, shows unambiguously the characteristic absorption of anthracene. Furthermore, two new maxima are reported at 408.5 and 372 nm, respectively. We have experimented that, in the absence of *N*-lithium diisopropylamide, 9-anthrylmethyl chloride reacted with SAN in such a way that the recovered polymer exhibited the same absorption as

that of Figure 8. As no reaction happened between 9-anthrylmethyl chloride and acetonitrile, it was obvious that the nitrile function was not concerned with the secondary reaction under investigation. From these observations, we have assumed that the polymer could be carrying some amine groups reactive towards chloride-containing compounds. This hypothesis was assessed by reacting 9-anthrylmethyl chloride with diethylamine. The UV–visible spectrum of the resulting quaternized product, i.e., Ⓐ$-CH_2-N(C_2H_5)_2H^+Cl^-$, is characterized by absorption maxima at 408.5; 387 and 367 nm, in good agreement with the spectrum of the reaction product between SAN and 9-anthrylmethyl chloride. Any significant excess in the 9-anthrylmethyl chloride over *N*-lithium diisopropylamide molar ratio is favorable to the occurrence of the quaternization reaction. Figure 9 supports convincingly that using equimolar amounts of Ⓐ$-CH_2Cl$ and $[(CH_3)_2CH]_2$ NLi is a sufficient condition to largely prevent it.

Once more, any attempt for extending to carbazole that alkylation pathway failed. The known halogenocarbazoles were synthesized by alkylating carbazole with an excess of a dihalogeno compound, under alkaline conditions.[32–35] In that way, 2-(*N*-carbazolyl) ethyl chloride and 4-(*N*-carbazolyl)butyl bromide were prepared and reacted with SAN in the conditions previously defined for 9-anthrylmethyl chloride. In any case, SAN was not labeled with carbazole, and this failure could be due to the dehydrohalogenation of the alkylating agent by the base present in the reaction medium. Of course, *N*-chloromethylcarbazole should be an attractive reagent, but no preparative method was found in the literature. Finally, the reaction of SAN with 2-(*N*-carbazolyl)ethylmagnesium bromide also failed as an alternative labeling pathway. The same result has previously been reported in the case of PMMA and tentatively attributed to the steric hindrance of the fluorescent chromophore.

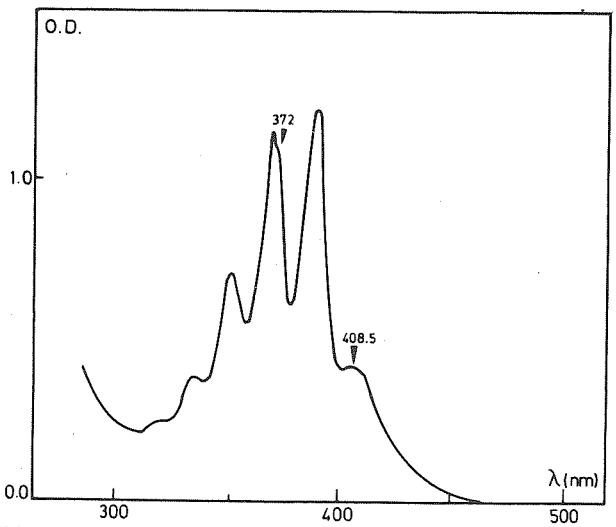


Fig. 8. UV–visible spectrum of SAN labeled by alkylation with a tenfold molar excess of 9-chloromethylanthracene over *N*-lithium diisopropylamide.

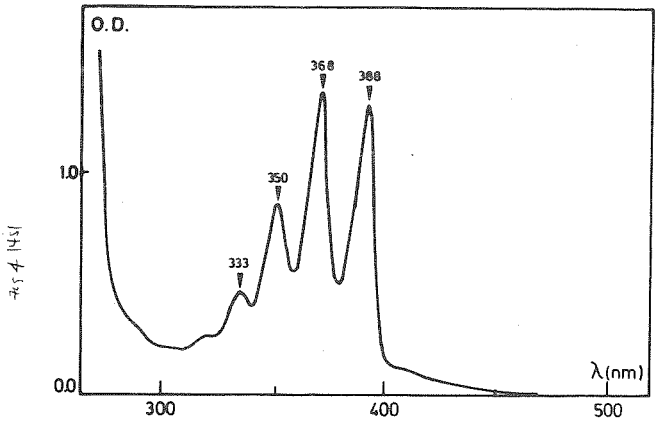


Fig. 9. UV–visible spectrum of SAN labeled by alkylation with equimolar amounts of 9-chloromethylanthracene and *N*-lithium diisopropylamide.

Labeling of PCL

The alkylation reaction, described in this paper for labeling SAN, is also pertinent to ester groups carrying an H atom at the α-position:

$$Y-CH_2-\overset{\overset{O}{\|}}{C}-OZ + BM \longrightarrow Y-\underset{M^+}{\overset{\ominus}{CH}}-\overset{\overset{O}{\|}}{C}-OZ + BH \qquad (13)$$

$$Y-\underset{M^+}{\overset{\ominus}{CH}}-\overset{\overset{O}{\|}}{C}-OZ + RX \longrightarrow Y-\underset{R}{CH}-\overset{\overset{O}{\|}}{C}-OZ + MX \qquad (14)$$

where RX is a halogeno compound and BM a strong and crowded base; in that respect *N*-lithium diisopropylamide is generally recommended for the alkylation of esters.[37,38] When this procedure was applied to PCL with 9-methylanthryl chloride as an alkylating agent, the polyester underwent severe chain scissions, even after a 5 mins reaction time at −20°C. The chain degradation is the consequence of the high sensitivity of PCL to basic reagents, and no efficient means could be devised to reduce it to satisfying limits. Up to now, no simple and direct technique works well for attaching fluorescent chromophores onto PCL, while avoiding the occurrence of secondary reactions.

The efficiency of some of the substitution techniques described hereabove allows a practical and clean labeling of existing polymers, and may represent an interesting tool for studying their phase situation in blends. A preliminary investigation of such potentialities in binary blends (s.PMMA/PVC and s.PMMA/SAN) is now in progress and will be extended to more complex systems containing block copolymers.

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References

1. O. Olabisi, L. E. Robeson, and M. T. Shaw, *Polymer–Polymer Miscibility,* Academic, New York, 1979.
2. D. S. Kaplan, *J. Appl. Polym. Sci.,* **20**, 2615 (1976).
3. D. L. Handlin, W. J. McKnight, and E. L. Thomas, *Macromolecules,* **14**, 795 (1981).
4. D. C. Douglass and V. J. McBrierty, *Macromolecules,* **11**, 766 (1978).
5. V. J. McBrierty, D. C. Douglass, and T. K. Kwei, *Macromolecules,* **11**, 1265 (1978).
6. B. Albert, R. Jerome, Ph. Teyssie, G. Smith, and V. J. McBrierty, *Macromolecules,* **17**, 2552 (1984).
7. B. Albert, R. Jerome, Ph. Teyssie, G. Smith, N. C. Boyle, and V. J. McBrierty, *Macromolecules,* **18**, 388 (1985).
8. B. Riedl, and R. E. Prud'Homme, *Polym. Eng. Sci.,* **24**, 1291 (1984).
9. J. Jelenic, R. G. Kirste, R. C. Oberthur, S. Schmitt-Strecker, and B. J. Schmitt, *Makromol. Chem.,* **185**, 129 (1984).
10. P. W. Schiller, in *Biochemical Luminescence,* R. F. Chen and E. Edolhoch, Eds., Dekker, New York, 1975, Vol. 2, chap. 5.
11. H. Morawetz and F. Amrani, *Macromolecules,* **11**, 281 (1978).
12. F. Amrani, J. M. Hung, and H. Morawetz, *Macromolecules,* **13**, 649 (1980).
13. F. Mikes, H. Morawetz, and K. S. Dennis, *Macromolecules,* **13**, 969 (1980).
14. H. Morawetz, *Ann. N. Y. Acad. Sci.,* **366**, 404 (1981).
15. F. Mikes, H. Morawetz, and K. S. Kennis, *Macromolecules,* **17**, 60 (1984).
16. K. C. Ramey, *J. Polym. Sci. B,* **5**, 859 (1967).
17. T. Ouhadi, C. Stevens, and Ph. Teyssie, *Makromol. Chem. Suppl.,* **1**, 191 (1975).
18. K. C. Schreiber and W. Emerson, *J. Org. Chem.,* **31**, 95 (1966).
19. E. Compaigne and W. L. Archer, *J. Am. Chem. Soc.,* **75**, 989 (1953).
20. P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.,* 1232 (1961).
21. J. M. Pearson, D. J. Williams, and M. Levy, *J. Am. Chem. Soc.,* **93**, 5478 (1971).
22. H. Gilman and F. K. Cartledge, *J. Organom. Chem.,* **2**, 447 (1964).
23. I. B. Berlman, *Energy Transfer Parameters of Aromatic Compounds,* Academic, New York, 1973.
24. J. V. Koleske and L. H. Wartman, *Poly(vinyl chloride),* McDonald Technical and Scientific, London, 1969.
25. F. J. Burgess, A. V. Cunliffe, J. R. McCallum, and D. H. Richards, *Polymer,* **18**, 719 (1977).
26. G. Lechermeier, Ph.D. Thesis, University of Lyon, France, 1976.
27. P. Rempp, J. Parrod, G. Laurent, and Y. Gallot, *C. R. Acad. Sci., Paris,* **260**, 903 (1965).
28. V. D. Daniels and N. H. Rees, *J. Polym. Sci. Polym. Chem. Ed.,* **12**, 2115 (1974).
29. E. D. Owen and I. Pasha, *J. Appl. Polym. Sci.,* **25**, 2417 (1980).
30. J. M. Pearson, D. J. Williams, and M. Levy, *J. Am. Chem. Soc.,* **93**, 5478 (1971).
31. A. Lagendijk and M. Szwarc, *J. Am. Chem. Soc.,* **93**, 5359 (1971).
32. G. R. Clemo and W. H. Perkin, *J. Chem. Soc.,* **125**, 1804 (1924).
33. J. Heller, D. L. Lyman, and W. A. Hewett, *Makromol. Chem.,* **73**, 48 (1964).
34. A. Barco, S. Benetti, and G. P. Pollini, *Synthesis,* **8**, 124 (1976).
35. V. Bocchi, G. Casnati, A. Dossena, and F. Villani, *Synthesis,* **8**, 414 (1976).
36. D. S. Watt, *Tetrahedron Lett.,* 707 (1974).
37. M. W. Rathke and A. Lindert, *J. Am. Chem. Soc.,* **125**, 1804 (1924).
38. R. J. Cregge, J. L. Hermann, C. S. Lee, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.,* 2425 (1973).

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