

by

Ph. Teyssié, R. Fayt, C. Jacobs, R. Jérôme, L. Leemans and S. Varshney
Laboratory of Macromolecular Chemistry, University of Liège
B6, SART TILMAN, 4000 LIEGE, BELGIUM

INTRODUCTION Alkyl(meth)acrylates (AMA) are becoming very important industrial monomers: although acrylonitrile still takes the lion's share in the acrylics production, i.e. over 3 millions tons per year, the esters (dominated by methylmethacrylate) represent another 2,5 millions (1). In particular, the attractive properties of polymethylmethacrylate (PMMA), such as clarity, higher T_g (ca. 130°C) when the syndiotactic content is increased, and potentialities of being combined with other materials, may foreshadow for it a bright future if efficient and low cost processes are available for production of the monomer.

In that prospect, the elegant demonstration by a Du Pont Co. research team that the nucleophile-assisted "group transfer" reaction of silylketene acetals could be turned into a well controlled "living" polymerization process for carbonyl-conjugated monomers (2) raised an extremely vivid interest among researchers interested in the molecular engineering of alkyl(meth)acrylates-based polymers and block copolymers. On the other hand, it also induced a second look at the sometimes difficult and therefore disregarded classical anionic polymerization of these monomers. It would indeed still be desirable to extend that latter type of "living" control, using simple and relatively low-cost initiators, to a high molecular weight range, and especially make it compatible with monomers lacking carbonyl-conjugated group such as dienes, styrenes and heterocyclic monomers, in order to easily synthesize the corresponding and still largely unknown block copolymers. The present paper will illustrate these points with a number of examples, which have further led to interesting and useful new materials.

I. ALK. METHACRYLATES The anionic homo- and block copolymerization of methacrylates, including functional ones, has been pretty well mastered by using specific conditions, i.e. low temperature (dry-ice), polar solvents (THF), and thorough monomer purification in particular from protic (alcohols) impurities, using aluminium alkyl complexes (3). When needed, the addition of a small amount of diphenyl-ethylene has provided the required stabilization of the living chain ends while changing the reaction conditions for block copolymerization (4). A very practical procedure involves the initial addition to the medium of some α -methylstyrene, which eventually caps the end of the first growing sequence and indicates by a color change the moment to start the synthesis of the second block (5). Many useful types of diblock copolymers have so been synthesized, and the properties of some recent ones are described below depending on their main use in heterophase materials molecular engineering.

Polymer-polymer blends The miscibility of PMMA with many other polymers "X" such as PVC, SAN, polycarbonate, PVDF, induced the idea that a poly(Y-b-MMA) block copolymer should be an efficient "emulsifier" to stabilize a fine dispersion of homopolymers X and Y, for example in melt-blended materials (6,7). A particularly useful type of such additives obtained along the route described above (5), are the poly(diene-b-MMA) copolymers, which can be used as such to produce extremely high impact PVC and SAN matrixes containing diene-based rubbers including Kratons (8), materials of which the failure profile can be somewhat tailored. Further hydrogenation of the diene block, leading to a polyolefin-like block (i.e. PHBD), allows now the preparation of other blends such as PVC/polyolefins, displaying f.i. good ageing characteristics (9).

Similar diblock copolymers but based on ter.butylmethacrylate instead of MMA, can be easily hydrolyzed into a product containing a carboxylic groups-rich block (h.tBMA), which can strongly interact with a number of other structures. An interesting application of that concept is the production of nylon-polystyrene (PS) blends using a P(S-b-h.tBMA) diblock (10), or of nylon-polyethylene (PE) blends with a P(HBD-b-

h.tBMA) one. The blends consist of a very fine phase dispersion, with extremely good interfacial adhesion, despite nylon crystallization. It is noteworthy that in all of the systems reported in this paper, relatively minor amounts of additive, i.e. a few weight percents, suffice to promote the desired effects, provided the structure of the additive has been well optimized.

Polymer-filler blends Similar interactions can be used of course to promote fine dispersion and adhesion in blends involving a polymer X and a filler, using an additive of the type P(X-b-h.tBMA), if the filler interacts well enough with carboxylic groups during processing (roll mill or extruder). Again, high loading with exceptional interfacial adhesion could be promoted that way, for example (7) in blends of CaCO₃ and polyethylene using the already mentioned P(HBD-h.tBMA) additive.

Polymer-liquid dispersions A very recent extension of those concepts allowed to solve, in a number of cases, the interesting question of dispersing small, submicron insoluble particles in a given liquid (pure, or polymer solution): the additive obviously has to contain one block which adsorbs or binds to the particle, and another one which gets solvated by the liquid and promotes the formation of a coalescence barrier. Two extreme examples illustrate the efficiency of that approach. The first one involves the stabilization of a pigment dispersion (1 μ carbon black particles) in a paraffin, thanks to a poly(styrene-b-stearylmethacrylate) diblock, for which an adsorption isotherm can be traced (11). The other example relies upon a poly(methylmethacrylate-b-glycidylmethacrylate) copolymer, the second block of which is then converted into a polysulfonic acid by reaction with sulfite. That additive ensures f.i. the complete stabilization of hydrophobic polyalkyl(meth)acrylate small particles (ca. 100 nm in size) transparent dispersions in an aqueous medium (12).

II. ALKYLACRYLATES: A CHALLENGE The anionic polymerization of these monomers is much more touchy and cannot be controlled by conventional anionic methods. Although different approaches can be taken to possibly meet that challenge (2, 13), answers have also been sought in the modification of classical anionic initiators, which are able at the same time to easily polymerize very different monomers including styrenes, dienes, heterocyclics, etc... It was thus proposed to minimize the relative importance of secondary transfer and termination reactions (usually ascribed to the presence of the unhindered carbonyl group and the α -acidic hydrogen), by creating enough steric hindrance around the propagating ion pair. Use of electronically well-balanced ligands is an obvious tactic here, and it appeared that μ -type hindering ligands, especially LiCl, were quite efficient (14) in controlling a perfectly "living", quantitative fast polymerization of hindered acrylates by lithium (ar)alkyls. The polymerization of ter.butylacrylate is a model of choice, on which the following characteristic features of "living" systems have been checked (15,16): linear dependence of \bar{M}_n on conversion, \overline{DP} equal to monomer over catalyst ratio, narrow M.W. distributions (\bar{M}_w/\bar{M}_n ca. 1.20), and complete resumption of additional monomer polymerization with the same characteristics (15). Li NMR spectroscopy confirmed the formation of a LiR:LiCl complex controlling the propagation process, and remaining efficient up to brine temperature in THF.

The possible applications of this type of initiators are obviously very broad, and the first one covers the synthesis of n.alkyl polyacrylates and of polyacrylic acid of predetermined M.W. and quite narrow M.W. distribution. The tert. butyl group of PtBMA is well-known indeed as a good leaving group in acid-catalyzed hydrolysis and transalcoholysis reactions. It was shown (1H NMR analysis, T_g measurements, acid-base titrations) that tert-butyl ester group could be converted nearly quantitatively into n.butyl or 2-ethylhexyl ones, or into carboxylic groups (14,15). "Random" acrylates copolymers can obviously be obtained by treatment with a mixture of alcohols.

Similarly, that approach can be applied to methacrylates polymerization by classical initiators when experimental conditions do not allow a good control of the "living" character. For example, MMA can be polymerized quantitatively at low temperature into a rather narrow symmetrical M.W. distri-

bution polymer (16), even when working in a low polarity medium (90:10 toluene/THF mixture).

It is also straightforward to terminate these "living" chains with a reaction leading to a functional group, i.e. reaction with CO₂ to yield a carboxylic end-group (14), etc... Finally, it is obvious that similar tBMA polymerizations can be initiated by polymer anions, i.e. polystyryl or polydienyl lithium, so producing diblock copolymers (14,17) which can also be eventually converted into the corresponding new n.alkylacrylate or acrylic acid block copolymers. Examples can be shown where a high efficiency is indeed attained (over 90 %).

IN CONCLUSION, it can certainly be said that recent achievements both in group-transfer polymerization and in controlled anionic polymerization of methacrylates and acrylates have paved the way for the molecular engineering of many new, interesting and hopefully useful products, which might ensure further development of that valuable class of monomers.

ACKNOWLEDGEMENT The authors gratefully acknowledge the support of IRSIA and SPPS national agencies (Brussels), as well as that of several industrial organizations (LABOFINA, SOLVAY, AGFA-GEVAERT, CIPARI, NORSOLOR).

REFERENCES

- (1) "La Chimie des Acryliques", p. 14, Techno-Nathan, Nouvelle Librairie S.A., Paris 1987
- (2) O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham and T.V. Rajan Babu, J. Am. Chem. Soc., 105 5706 (1983)
- (3) R.D. Allen, T.E. Long and J.E. Mc Grath, Polymer Bulletin, 15, 127 (1986)
- (4) See for example G.D. Andrews and L.R. Melby, in "New Monomers and Polymers", B.M. Culbertson and C.U. Pittmann Jr. Ed., Plenum Press, 357 (1984); M. Leng, D. Freyss P. Rempp, Bull. Soc. Chim. France, 211 (1964)
- (5) Ph. Teyssié, R. Jérôme, T. Ouhadi, R. Fayt, U.S. Pat., 4,461,874, Jul. 24, 1984
- (6) Ph. Teyssié et al., in ACS Sym. Series Nr. 59, T. Saegusa and E. Goethals Ed., 174 (1977)
- (7) Ph. Teyssié, Makromol. Chem., Symposia, Strasbourg, May 1987, and Lyon, September 1987, in press.
- (8) R. Fayt and Ph. Teyssié, Macromolecules 19 2077 (1986)
- (9) R. Fayt and Ph. Teyssié, submitted to J. Polym. Sci., Phys. Ed.
- (10) R. Fayt, Ph. Teyssié, D. Hanton, French Pat., 2,582,659 June 3, 1985; R. Fayt, R. Jérôme and Ph. Teyssié, Polym. Eng. Sci., 27, 328 (1987)
- (11) L. Leemans, R. Fayt, N. de Jaeger and Ph. Teyssié, submitted to Polymer; see also (7).
- (12) L. Leemans, H. Uytterhoeven, Ph. Teyssié, R. Fayt, N. de Jaeger, submitted to J. Polym. Sci., Chem. Ed.; *ibid.*, patents pending.
- (13) See for example A.H.E. Müller, L. Lochmann, J. Trekoval, Makromol. Chem., 187, 1473 (1986); Brit. Pat. 882,586 to Rohm and Haas Co., Nov. 15, 1961; see also references in (15).
- (14) T. Ouhadi, R. Forte, R. Jérôme, R. Fayt, Ph. Teyssié, Luxembourg Patent 85,627, Nov. 5, 1984
- (15) R. Fayt, R. Forte, C. Jacobs, R. Jérôme, T. Ouhadi, Ph. Teyssié and S.K. Varshney, Macromolecules, 20, 1442 (1987)
- (16) R. Jérôme, R. Forte, S.K. Varshney, R. Fayt, Ph. Teyssié, in "Recent Advances in Mechanistic and Synthetic Aspects of Polymerization", M. Fontanille and A. Guyot Ed., D. Reidel Publ. Co., 101 (1987)
- (17) R. Forte, T. Ouhadi, R. Fayt and Ph. Teyssié, submitted to J. Polym. Sci., Polym. Chem. Ed.